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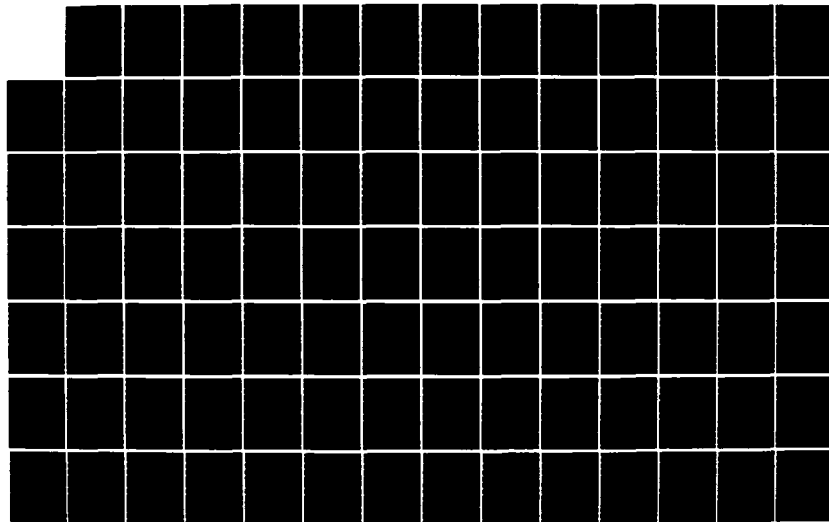   COLUMBUS OHIO ON 16-20 JUNE 1986(U) OHIO STATE UNIV
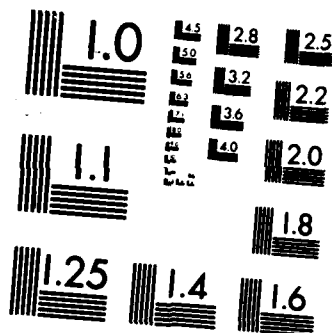   COLUMBUS DEPT OF CHEMISTRY   21 JUN 86

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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

Forty-First

symposium on

MOLECULAR SPECTROSCOPY

JUL 1 1 1986

THE OHIO STATE UNIVERSITY

JUNE 16-20, 1986

UNDER THE SPONSORSHIP OF
THE DEPARTMENT OF PHYSICS
THE DEPARTMENT OF CHEMISTRY
THE GRADUATE SCHOOL
THE OFFICE OF ACADEMIC AFFAIRS
OF THE UNIVERSITY
AND
THE U.S. ARMY RESEARCH OFFICE
THE U.S. AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

OCT 2 3 1986

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INFORMATION

ACCOMMODATIONS: The check-in for dormitory accommodations is located in Drackett Tower (6) on Curl Drive. Curl Drive is a one-way street going north from West Woodruff Avenue.

BANQUET: This will take place at the Faculty Club (8) on Wednesday, June 18, 1986.
RECEPTION: 6:30-7:30 p.m. BANQUET: 7:30 p.m. Nobel Laureate Philip W. Anderson, Princeton University, Princeton, New Jersey, will be the speaker.

MAIL: Address your mail for delivery during the Symposium to: c/o MOLECULAR SPECTROSCOPY SYMPOSIUM, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio, 43210, U.S.A.

PARKING: Please purchase your parking permits when you check into the dorms or at the Registration Desk. These permits allow you to park in the Tuttle-Woodruff parking lot only. The permits must be displayed on the front windshield of your car. Please follow all traffic rules to avoid the issuance of tickets.

REGISTRATION: The Registration Desk will be located in Room 1036, Physics Laboratory. It will be kept open between 8:30 a.m.--noon and 1:00--4:30 p.m., Monday through Friday. The registration fee is $60.00 per participant and $50.00 if paid by June 1. The special rate of $20.00 per Graduate Student will be reduced to $18.00 if paid by June 1. Please send the completed registration form along with your check by June 1.

SESSIONS: They will be held in: Independence Hall (2), Physics Lab (4), and Evans Chemical Lab (5). Digits in parentheses correspond to the campus map below:

West Woodruff Ave.
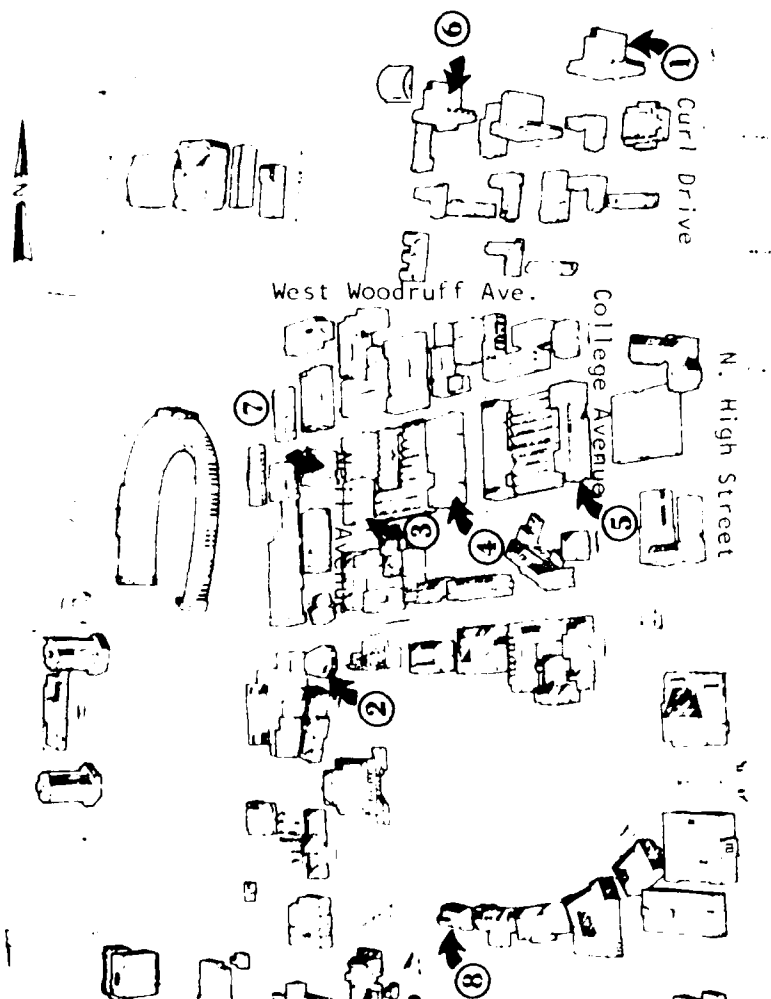
THE OHIO STATE UNIVERSITY

1   Taylor Tower

2   Independence Hall

3   Post Office

4   Physics Laboratory
     (Smith Lab.)

5   Evans Laboratory

6   Drackett Tower
     (Check-In)

7   Electronics Laboratory

8   Faculty Club

PLANS FOR THE 42ND SYMPOSIUM (JUNE 15-19, 1987)

So far, the Invited Speakers are:

K. M. EVENSON, NATIONAL BUREAU OF STANDARDS, COLORADO

WILLIAM KLEMPERER, HARVARD UNIVERSITY

R. H. SCHWENDEMAN, MICHIGAN STATE UNIVERSITY

ŠTEPAN URBAN, CZECHOSLOVAK ACADEMY OF SCIENCES

We expect to have special emphasis on the Van der Waals
molecules at this conference. Alfons Weber, National
Bureau of Standards, pointed out the timeliness of
considering this subject at the 1987 Symposium. It may
be mentioned that the Proceedings of the NATO Workshop
organized by A. Weber on the same topic scheduled to be
held in Europe later this year will appear in print by
about June 1987.

In some recent discussions with Mary Ann Smith and C. P.
Rinsland of NASA-Langley, it became evident that suffi-
cient interest exists for holding a Specially Arranged
Seminar on "Probing and Modeling the Earth's Atmosphere"
during the June 1987 Molecular Symposium here. So far,
Linda R. Brown of the Jet Propulsion Laboratory has
accepted to be one of the Invited Speakrs at this seminar.

A-1

THIS DIMENSION SHOULD BE 6 in. (≈15 cm) or less

HIGH RESOLUTION FOURIER SPECTROSCOPY OF THE Ar^+ LASER 5145 Å EXCITED I_2 FLUORESCENCE SPECTRUM

R. BACIS, S. CHURASSY, R. W. FIELD, J. B. KOFFEND, AND J. VERGES

This preliminary work demonstrates the feasibility of obtaining a high resolution spectrum of cw laser excited fluorescence using a Fourier spectrometer.

Using 1.3W of 5145 Å multimode power from an Ar^+ laser, fluorescence is excited mainly via the P(13) and R(15) (43,0) lines. Nearly all of the ~~' fluorescence lines [P(13), P(17), R(11), R(15)] originating from v' = 43 are observed 85. Their recorded full width at half maximum in the 7000-8000 cm^{-1} regi~

Rotational relaxation (ΔJ' -   rous odd-J" satellite lines. The usual parameters are obtain.   rotation-vibration levels of I_2 $X^1\Sigma^+$ through v" = 85.

This sample abstract gives the required format

The vibrational line intens~   ~~ the alternation pattern predicted by the Franck-Condon factors of Tellingh.   ~ne agreement between measured and calculated intensities is only qualitative for ~~gh v" values. This has important implications with respect to the I_2 laser gain measurements discussed in the following talk.

Will be copied photographically

---

[1] J. Tellinghuisen, J. Quant. Spect. Rad. Transf. <u>19</u>, 149 (1978).

Address of Bacis and Churassy: Laboratoire de Spectrométrie Ionique et Moléculaire 43, bd du 11 Novembre 1918, 69621 - Villeurbanne, France.
Address of Field and Koffend: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.
Address of Verges: Laboratoire Aimé Cotton - C.N.R.S. II, Bâtiment 505, 91405 - Orsay, France.

Time required: 15, 10 or 5 min.

✱ Session in which paper is recommended for presentation:_____

Chemical formulas & sketches of molecular structures for larger molecules:

PLEASE NOTE:
1. Use good quality bond paper and an electric typewriter when preparing your Abstract. In the space for title and abstract you may include tables, equations and line drawings.

2. Send an original and one copy.

3. Please use a larger envelope for mailing. Do not fold.

4. Underline the name of the person who will be presenting the paper.

5. Include only the TITLE, AUTHORS' NAMES, and TEXT in the abstract. The author's affiliation should be given separately, as shown in the example.

6. Supply chemical formulas and rough sketches of structures of the larger molecules. This information is useful in arranging sessions.

General categories of sessions:

(1) Electronic (large molecules)   (6) Laser spectra   (11) Raman spectra
(2) Electronic (small molecules)   (7) Liquid state   (12) Solid state (electronic)
(3) Electronic (theory)   (8) Matrix spectra   (13) Solid state (infrared)
(4) Energy transfer   (9) Microwave   (14) Techniques
(5) High resolution IR & THEORY   (10) Molecular beam   (15) Vibrational analysis

PLEASE CHOOSE ONE OF THESE FIFTEEN CATEGORIES FOR YOUR PAPER AND GIVE THAT INFORMATION IN THE PLACE WHERE THE ✱ APPEARS ABOVE. THANK YOU.

MONDAY, JUNE 16, 1986 -- 9:15 A.M.

Auditorium, Independence Hall

Chairmen: S. LESLIE BLATT, Department of Physics,
The Ohio State University, Columbus, Ohio.

L. A. NAFIE, Department of Chemistry,
Syracuse University, Syracuse, New York.

Partial ( )

Plenary Session

MA1. INFRARED SPECTROSCOPY OF MOLECULAR IONS ....40 min.

TAKESHI OKA, Department of Chemistry and
Department of Astronomy and Astrophysics,
The University of Chicago, Chicago, Illinois,
60637.

MA2. EVALUATIONS OF MOLECULAR CONSTANTS -- A CONTINUING
SEARCH FOR PROPER PROCEDURES AND PERSPECTIVES.............40 min.

C. WELDON MATHEWS, Department of Chemistry,
The Ohio State University, Columbus, Ohio,
43210.

COBLENTZ PRIZE AND AWARD LECTURE (11:00 A.M.--12:00 NOON)

MA3. PHOTOTHERMAL METHODS FOR ANALYTICAL LASER SPECTROSCOPY...40 min.

J. M. HARRIS, Department of Chemistry,
University of Utah, Salt Lake City,
Utah, 84112.

PLEASE NOTE:

ALL PAPERS IN THE Σ AND Π SESSIONS HAVE BEEN SCHEDULED
FOR PRESENTATION. THE LISTS OF THESE LATE PAPERS APPEAR ON
PAGE 34 FOR Σ AND PAGES 35-36 FOR Π. THE ABSTRACTS FOR THESE
PAPERS HAVE BEEN INCLUDED IN THE SESSIONS IN WHICH THE PAPERS
ARE ACTUALLY BEING PRESENTED. THE LOGISTICS INVOLVED IN
THE PREPARATION OF THE PROGRAM AND ABSTRACTS NECESSITATED
THIS PROCEDURE. IF THERE IS ANY CONFUSION, PLEASE SPEAK TO
ME.

THANK YOU. *Rao*

MONDAY, JUNE 16, 1986 — 1:30 P.M.

Room 1153, Physics Laboratory

Chairman: T. J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York.

ME1. A MULTIPLE REFLECTION CELL TO ENHANCE DIRECT IR ABSORPTION IN A COLLIMATED MOLECULAR BEAM...10 min.(1:30)

> D. KAUR, A. M. DE SOUZA, and D. S. PERRY, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

ME2. HIGH RESOLUTION INFRARED SPECTROSCOPY OF LiCl AT 800°C......................15 min.(1:42)

> G. A. THOMPSON, A. G. MAKI, WM. B. OLSON, and A. WEBER, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

ME3. HIGH RESOLUTION SPECTRUM OF THE ν_2 AND $2\nu_6$ BANDS OF ^{28}SiH$_3$D.................15 min.(1:59)

> R. D. SCHAEFFER, R. W. LOVEJOY, Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania, 18015; W. B. OLSON, Molecular Spectros opy Division, National Bureau of Standards, Gaithersburg, Marylana, 20899; and G. TARRAGO, Laboratoire D'Infrarouge, Universite de Paris-Sud, Campus d'Orsay, 91405 Orsay, France.

ME4. ANALYSIS OF THE ν_{14} BAND OF BENZENE-d$_6$......................................15 min.(2:16)

> J. PLIVA, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania, 16802; A. VALENTIN, J. CHAZELAS, and L. HENRY, Laboratoire de Spectronomie Moleculaire CNRS 060136, Universite Pierre et Marie Curie, 75230 Paris, France.

ME5. REFILLING TRANSITIONS IN TEA-PUMPED METHANOL FIR LASERS.....................15 min.(2:33)

> I. MUKHOPADHYAY, R. M. LEES, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada, E3B 5A3; and J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

ME6. THE THREE LOWEST-LYING FUNDAMENTALS OF AMINOBORANE, NH$_2$BH$_2$.................15 min.(2:50)

> W. D. ANDERSON, M.C.L. GERRY, L. LEWIS-BEVAN, A. J. MERER, and D. M. STEUNENBERG, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Y6.

ME7. DIODE LASER SPECTRA AND ANALYSIS OF THE $\nu_1-\nu_3$ BAND OF CF$_3{}^{35}$Cℓ..............10 min.(3:07)

> S. GIORGIANNI, R. VISINONI, A. GAMBI, S. GHERSETTI, Dipartimento di Spettroscopia, Elettrochimica e Chimica Fisica, Universita di Venezia, I-30123 Venezia, Italy; A. BIZZARRI, J. HERMANUSSEN, and G. BALDACCHINI, ENEA, TIB, Divisione Fisica Applicata, 00044 Frascati, Rome, Italy.

Intermission

ME8. STARK AND ZEEMAN EFFECT OF ETHYLENE OBSERVED BY SUB-DOPPLER INFRARED SPECTROSCOPY..15 min.(3:30)

> YIT-TSONG CHEN and TAKESHI OKA, Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois, 60637.

ME9. MAGNETIC FIELD MODULATED INFRARED LASER SPECTROSCOPY OF THE ClH$_2{}^+$ ν_2 BAND..10 min.(3:47)

> K. KAWAGUCHI and E. HIROTA, Institute for Molecular Science, Okazaki 444, Japan.

ME10. INFRARED DIODE LASER SPECTROSCOPY OF THE HYDROGEN BIFLUORIDE ANION: FHF$^-$ AND FDF$^-$...15 min.(3:59)

> K. KAWAGUCHI and E. HIROTA, Institute for Molecular Science, Okazaki 444, Japan.

ME11. CALCULATED SPECTROSCOPIC PROPERTIES OF HBF$^+$ AND HBCl$^+$......................10 min.(4:16)

> P. BOTSCHWINA, Fachbereich Chemie der Universität Kaiserslautern, D-6750 Kaiserslautern, West Germany.

ME12. CALCULATED SPECTROSCOPIC PROPERTIES OF SOME SMALL POLYATOMIC ANIONS.........15 min.(4:28)

> P. BOTSCHWINA, Fachbereich Chemie der Universität Kaiserslautern, D-6750 Kaiserslautern, West Germany.

ME13. Π6 will be presented here (HOWARD COKER)...................................10 min.(4:45)

ME14. Π9 will be presented here (E. A. COHEN).............. ....10 min.(4:57)

MONDAY, JUNE 16, 1986 — 1:30 P.M.

Room 1009, Physics Laboratory

Chairman: GRANT BICKEL, Department of Chemistry, State University of New York,
University Center at Binghamton, Binghamton, New York.

MF1. MEASURED RADIATIVE LIFETIMES FOR H_2 AND HD IN THE E,F $^1\Sigma_g^+$ ELECTRONIC STATE..10 min.(1:30)

D. W. CHANDLER and L. R. THORNE, Combustion Research Facility,
Sandia National Laboratories, Livermore, California, 94550.

MF2. SCHUMANN-RUNGE ABSORPTION BANDS OF $^{16}O^{18}O$.................................10 min.(1:42)

K. YOSHINO, D. E. FREEMAN, and W. H. PARKINSON, Harvard-
Smithsonian Center for Astrophysics, 60 Garden St., Cambridge,
Massachusetts, 02138.

MF3. HIGH RESOLUTION CROSS SECTIONS AND BAND OSCILLATOR STRENGTHS OF THE
SCHUMANN-RUNGE BANDS OF ISOTOPIC OXYGEN..................................15 min.(1:54)

K. YOSHINO, D. E. FREEMAN, J. R. ESMOND, and W. H. PARKINSON,
Harvard-Smithsonian Center for Astrophysics, 60 Garden St.,
Cambridge, Massachusetts, 02138.

MF.4. AN ELECTRIC QUADRUPOLE TRANSITION: The b $^1\Sigma_g^+$ - a $^1\Delta_g$ EMISSION
SYSTEM OF OXYGEN..10 min.(2:11)

E. H. FINK, H. KRUSE, Physikalische Chemie-Fachbereich 9,
Bergische Universität-Gesamthochschule Wuppertal, D-5600
Wuppertal 1, Federal Republic of Germany; D. A. RAMSAY, and
M. VERVLOET, Herzberg Institute of Astrophysics, National
Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

MF5. NEAR-INFRARED EMISSION SPECTRA OF S_2 AND SeS...........................10 min.(2:23)
E. H. FINK, H. KRUSE, Physikalische Chemie-Fachbereich 9,
Bergische Universität- Gesamthochschule Wuppertal, D-5600 Wuppertal 1,
Federal Republic of Germany; D. A. RAMSAY, and D. C. WANG, Herzberg
Institute of Astrophysics, National Research Council of Canada,
Ottawa, Ontario, Canada, K1A OR6.

MF6. REINVESTIGATION OF THE E,F+X SYSTEMS OF S_2...............................10 min.(2:35)

C. G. MAHAJAN, Department of Physics, Punjab University, Chandigarh --
160014, India. Current Address: Department of Physics, University
of Toronto, Toronto, Ontario, Canada, M5S 1A7.

Intermission

MF7. HIGH RESOLUTION FOURIER TRANSFORM EMISSION SPECTROSCOPY OF CP AND PH.......15 min.(3:00)

R. S. RAM and P. F. BERNATH, Department of Chemistry, University
of Arizona, Tucson, Arizona, 85721.

MF8. ROTATIONAL LINE INTENSITIES IN THE $b^1\Sigma^+$ - $X^3\Sigma^-$ SYSTEM OF THE NF MOLECULE....10 min.(3:17)

M. VERVLOET and J.K.G. WATSON, Herzberg Institute of Astrophysics,
National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

MF9. RADIATIVE LIFETIMES OF THE O_u^- SUBLEVELS OF THE RARE GAS EXCIMERS...........15 min.(3:29)

DAVID L. HUESTIS, Chemical Physics Laboratory, SRI International,
Menlo Park, California, 94025.

MF10. HIGH-RESOLUTION VUV LASER-EXCITED SPECTRA OF Ar_2........................15 min.(3:46)

P. R. HERMAN and B. P. STOICHEFF, Department of Physics, University
of Toronto, Toronto, Ontario, Canada, M5S 1A7.

MF11. THE $B^2\Sigma^+$-$X^2\Sigma^+$ SYSTEM OF $^{12}C^{16}O^+$ AND $^{13}C^{16}O^+$.....................10 min.(4:03)

P. MISRA, D. W. FERGUSON, K. NARAHARI RAO, Department of Physics,
The Ohio State University, Columbus, Ohio, 43210; and C. WELDON MATHEWS,
Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

MF12. ZEEMAN SPLITTING OF THE $A^1\Sigma_u^+ \sim b^3\Pi_u$ PERTURBED LEVELS OF $^6Li_2$...............15 min.(4:15)

R. A. BERNHEIM, L. P. GOLD, W-H. JENG, and X. XIE, Department
of Chemistry, The Pennsylvania State University, University Park,
Pennsylvania, 16802.

MF13. FLUORESCENCE QUENCHING IN THE $B^3\Pi_{0^+u}$ STATE OF I_2.........................15 min.(4:32)

B. R. REDDY and S. PADDI REDDY, Department of Physics, Memorial
University of Newfoundland, St. John's, Newfoundland, Canada, A1B 3X7.

MF14. Π7 will be presented here (B. D. McFEETERS)...............................15 min.(4:49)

MONDAY, JUNE 16, 1986 -- 1:30 P.M.

Room 1005, Physics Laboratory

CHAIRMAN: J. J. HILLMAN, Laboratory for Extraterrestrial Physics, NASA/Goddard Space Flight Center, Greenbelt, Maryland.

MG1.   MOLECULAR PARAMETERS FOR CARBON DIOXIDE ABSORPTIONS IN THE 3450 cm^{-1} SPECTRAL REGION.. 5 min.(1:30)

D. CHRIS BENNER, V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; and CURTIS P. RINSLAND, NASA/Langley Research Center, MS 401A, Hampton, Virginia, 23665.

MG2.   SENSITIVITY OF BAND INTENSITIES OF CO_2 TO EXPERIMENTAL DATA IN DIRECT NUMERICAL DIAGONALIZATION CALCULATIONS...............................15 min.(1:37)

RICHARD B. WATTSON, Visidyne, Inc., 10 Corporate Place, S. Bedford St., Burlington, Massachusetts, 01803; and LAURENCE S. ROTHMAN, Optics Division, Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 01731.

MG3.   THE NEW VERSION OF THE HITRAN DATABASE: EXAMPLE OF CARBON DIOXIDE LINE PARAMETERS.. 15 min.(1:52)

LAURENCE S. ROTHMAN, Optics Division, Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 01731; RICHARD B. WATTSON, Visidyne, Inc., 10 Corporate Place, S. Bedford St., Burlington, Massachusetts, 01803; and ROBERT R. GAMACHE, Center for Atmospheric Research, University of Lowell, Lowell, Massachusetts, 01854.

MG4.   LINE POSITIONS AND LINE STRENGTHS OF CO_2 BANDS IN THE 750 TO 1100 cm^{-1} REGION..10 min.(2:09)

L. R. BROWN, Jet Propulsion Laboratory, MS 183-301, 4800 Oak Grove Drive, Pasadena, California, 91109.

MG5.   LINE POSITIONS OF $\Delta v_3 = 1$ BANDS OF $^{12}C^{16}O^{18}O$................................10 min.(2:21)

MARK P. ESPLIN, Stewart Radiance Laboratory, Utah State University, Bedford, Massachusetts, 01730; and JOHN P. MYCROFT, Optical Physics Division, United States Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 01731.

MG6.   THE LASER QUANTITATIVE SPECTRA OF DIOXIDE CARBON AT 10μ BANDS............... 5 min.(2:33)

CAI PEIPEI, SHEN SHANXIONG, ZHANG HANSHENG, and I-SHAN ZHENG, Department of Physics, East-China Normal University, Shanghai, 200062, People's Republic of China.

MONDAY, JUNE 16, 1986 — 2:45 P.M.

Room 1005, Physics Laboratory

Chairman: DAVID S. PERRY, Department of Chemistry, University of Rochester, Rochester, New York.

MG'1. VIBRATIONAL ASSIGNMENTS OF BANDS RESOLVED BY LOW TEMPERATURE, MATRIX ISOLATION TECHNIQUES..15 min.(2:45)

  D. PRESSER, F. M. WASACZ, Mattson Instruments, Inc., 6333 Odana Road, Madison, Wisconsin, 53719; and R. J. JAKOBSEN, Mattson Institute for Spectroscopic Research, 326 Walhalla Road, Columbus, Ohio, 43202.

MG'2. EMISSION SPECTRA FOR MATRIX ISOLATED IF: OBSERVATION OF A NEW LOW LYING ELECTRONIC STATE...15 min.(3:02)

  J. P. NICOLAÏ and M. C. HEAVEN, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, 60616.

MG'3. COMPARISON OF THE ELECTRONIC ENERGY LEVELS OF DIATOMIC MOLECULES IN THE GAS PHASE AND IN INERT SOLID MATRICES.............................15 min.(3:19)

  MARILYN E. JACOX, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

MG'4. THE A $^2\Pi$ - X $^2\Sigma^+$ NEAR INFRARED ABSORPTION SPECTRUM OF HC_2 ISOLATED IN SOLID ARGON...15 min.(3:36)

  MARILYN E. JACOX, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

MG'5. COLOR CENTER LASER SPECTROSCOPY OF C_2D AND C_2H.......................15 min.(3:53)

  W-B. YAN, C. B. DANE, JEFFREY L. HALL, and R. F. CURL, Department of Chemistry and Rice Quantum Institute, Rice University, Houston, Texas, 77251.

MG'6. FTIR ISOTOPIC STUDY OF C_2H IN AN ARGON MATRIX..........................15 min.(4:10)

  RICHARD A. SHEPHERD and W.R.M. GRAHAM, Department of Physics, Texas Christian University, Fort Worth, Texas, 76129.

MG'7. HYPERFINE AND QUADRUPOLE PARAMETERS OF THE MnH MOLECULE....................10 min.(4:27)

  R. J. VAN ZEE, D. A. GARLAND, and W. WELTNER, JR., Department of Chemistry, University of Florida, Gainesville, Florida, 32611.

MG'8. GROUND STATES AND HYPERFINE PARAMETERS FOR SOME TRANSITION-METAL CARBIDE MOLECULES..10 min.(4:39)

  J. J. BIANCHINI, R. J. VAN ZEE, and W. WELTNER, JR., Department of Chemistry, University of Florida, Gainesville, Florida, 32611.

MG'9. Π5 will be presented here (V. E. BONDYBEY)..................................10 min.(4:51)

TUESDAY, JUNE 17, 1986 — 8:30 A.M.

Room 1153, Physics Laboratory

WALTER GORDY MEMORIAL

Chairman Before Intermission: FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina.

Chairman After Intermission: P. BOTSCHWINA, Fachbereich Chemie der Universität, Kaiserslautern, D-6750 Kaiserslautern, West Germany.

"WALTER GORDY".. (8:30)

> FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

TA1. TRICARBON OXIDE SULFIDE, $O=C=C=C=S$, REVISITED.................................15 min.(8:40)

> M. WINNEWISSER and F. HOLLAND, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-6300 Giessen, Federal Republic of Germany.

TA2. NEW METHODS IN STRUCTURE DETERMINATION UTILIZING GROUND STATE ROTATIONAL CONSTANTS...15 min.(8:57)

> MARLIN D. HARMONY and WILLIAM H. TAYLOR, Department of Chemistry, University of Kansas, Lawrence, Kansas, 66045.

TA3. MICROWAVE SPECTRUM, STRUCTURE AND DIPOLE MOMENT OF METHYLENECYCLOPROPENE....15 min.(9:14)

> W. H. TAYLOR, M. D. HARMONY, Department of Chemistry, University of Kansas, Lawrence, Kansas, 66045; T. D. NORDEN, and S. W. STALEY, Department of Chemistry, University of Nebraska, Lincoln, Nebraska, 68588.

TA4. OXYGEN-17 QUADRUPOLE COUPLING IN OPF_3 BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY..10 min.(9:31)

> J. MATOS, K. W. HILLIG II, and R. L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

TA5. THE MICROWAVE SPECTRUM AND CONFORMATION OF METHOXY OZONIDE $(H_3COCHOOCH_2O)$...10 min.(9:43)

> M. SOLTIS LABARGE, R. L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109; and H. KEUL, Lehrstuhl für Textilchemie und Makromoleculare Chemie, der RWTH, Aachen, West Germany.

TA6. THE MICROWAVE SPECTRUM OF BISOXIRANE......................................10 min.(9:55)

> C. F. SU, R. L. COOK, Department of Physics and Astronomy, Mississippi State University, Mississippi State, Mississippi, 39762; and V. F. KALASINSKY, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi, 39762.

Intermission

TA7. THE MILLIMETER AND SUBMILLIMETER WAVE SPECTRA OF CF^+ AND H_3O^+...............15 min.(10:25)

> GRANT M. PLUMMER, TODD ANDERSON, ERIC HERBST, and FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

TA8. FREQUENCY TUNABILITY IN A SMALL OPTICALLY PUMPED FAR INFRARED LASER.........15 min.(10:42)

> HENRY EVERITT and FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

TA9. FREQUENCY MEASUREMENT OF FIR LASING TRANSITIONS............................15 min.(10:59)

> RICHARD L. CROWNOVER, FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706; DAVID D. SKATRUD, United States Army Research Office, Research Triangle Park, North Carolina, 27709; and K V.L.N. SASTRY, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada, E3B 5A3.

TA10. THE FAR INFRARED SPECTRA AND CONFORMATIONAL STABILITY OF 3-CHLOROPROPENE AND 3-CHLORO-2-METHYL-PROPENE...15 min.(11:16)

> D. T. DURIG, T. S. LITTLE, and J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

TA11. FAR INFRARED SPECTRA AND CONFORMATIONAL STABILITY OF FCH_2CFO, FCH_2CClO, AND FCH_2CBrO...15 min.(11:33)

H. PHAN, T. S. LITTLE, and J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

TA12. MILLIMETER WAVE SPECTROSCOPY OF H–CCC–H ISOTOPOMERS DETERMINATION OF THE r_s STRUCTURE................................Arrived Late...................10 min.(11:50)

M. BOGEY, C. DEMUYNCK, and J. L. DESTOMBES, Laboratoire de Spectroscopie Hertzienne, CNRS, Université de Lille I, Villeneuve d'Ascq, France.

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TUESDAY, JUNE 17, 1986 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chairwoman: LINDA R. BROWN, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, California.

TB1. A LOW-TEMPERATURE ABSORPTION CELL FOR FTS AND DIODE LASER SPECTROSCOPY OF GASES..10 min.(8:30)

D. E. JENNINGS, G. W. HALSEY, and J. J. HILLMAN, Planetary Systems Branch, Code 693.2, NASA/Goddard Space Flight Center, Greenbelt, Maryland, 20771.

TB2. TEMPERATURE DEPENDENCE OF THE H_2-BROADENING COEFFICIENT FOR THE ν_9 FUNDAMENTAL OF ETHANE...10 min.(8:42)

J. J. HILLMAN, G. W. HALSEY, and D. E. JENNINGS, Planetary Systems Branch, Code 693.2 and Laboratory for Extraterrestrial Physics, NASA/Goddard Space Flight Center, Greenbelt, Maryland, 20771.

TB3. DETERMINATION OF THE $^{16}O^{12}C^{32}S$ ν_3-FUNDAMENTAL BAND STRENGTH FROM DIODE LASER MEASUREMENTS...10 min.(8:54)

T. E. BLACKBURN, C. CHACKERIAN, JR., M. LOEWENSTEIN, and J. R. PODOLSKE, NASA/Ames Research Center, MS 245-5, Moffett Field, California, 94035.

TB4. MEASUREMENT OF HYDROGEN-BROADENED LINE WIDTHS OF CO AT LOW TEMPERATURES.....15 min.(9:06)

P. VARANASI, S. CHUDAMANI, and S. KAPUR, Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, New York, 11794-2300.

TB5. AIR-BROADENED HALFWIDTHS IN THE ν_3 BAND OF $^{12}CH_4$............................10 min.(9:23)

D. CHRIS BENNER, V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; and CURTIS P. RINSLAND, NASA/Langley Research Center, MS 401A, Hampton, Virginia, 23665.

TB6. ABSOLUTE LINE INTENSITIES OF NO AND PRESSURE BROADENING COEFFICIENTS FOR NO-N_2 MIXTURES..15 min.(9:35)

T. G. NEISS, R. W. LOVEJOY, Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania, 18015; and C. CHACKERIAN, JR., Astrophysics Experiments Branch, NASA/Ames Research Center, Moffett Field, California, 94035.

TB7. NEW INFRARED FREQUENCY AND INTENSITY MEASUREMENTS ON CHLORINE MONOXIDE (ClO)...15 min.(9:52)

J. B. BURKHOLDER, P. D. HAMMER, C. J. HOWARD, NOAA Environmental Research Laboratories, 325 Broadway, Boulder, Colorado, 80303; A. G. MAKI, G. THOMPSON, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899; and C. CHACKERIAN, NASA/Ames Research Center, Moffett Field, California, 94035.

Intermission

TB8. THE INTENSITY AND SELF-BROADENING OF OVERTONE TRANSITIONS IN HCN............15 min.(10:25)

A. M. SMITH, W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138; and K. K. LEHMANN, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

TB9. AN INTERPRETATION OF INFRARED INTENSITIES OF POLYATOMIC MOLECULES...........15 min.(10:42)

WILLIS B. PERSON, Department of Chemistry, University of Florida, Gainesville, Florida, 32611.

TB10. CONCENTRATION INDEPENDENT ABSOLUTE INTENSITY DETERMINATIONS: A NEW METHOD.10 min.(10:59)

C. CHACKERIAN, JR., NASA/Ames Research Center, MS 245-6, Moffett Field, California, 94035.

TB11. N_2 AND AIR BROADENING IN THE FUNDAMENTAL BANDS OF HF AND HCl................15 min.(11:11)

A. S. PINE, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899; and J. P LOONEY, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania, 16802.

TUESDAY, JUNE 17, 1986 — 8:30 A.M.

Room 1005, Physics Laboratory

Chairman Before Intermission: PETER BERNATH, Department of Chemistry, University of Arizona, Tucson, Arizona.

Chairman After Intermission: KEVIN K. LEHMANN, Department of Chemistry, Princeton University, Princeton, New Jersey.

TC1. LASER-INDUCED PHOSPHORESCENCE SPECTROSCOPY IN SUPERSONIC JETS. THE LOWEST TRIPLET STATES OF GLYOXAL, METHYLGLYOXAL, AND BIACETYL......................15 min.(8:30)

L. H. SPANGLER, Los Alamos National Laboratory, MS-G738, Los Alamos, New Mexico, 87545; and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

TC2. ROTATIONAL ANALYSIS OF SOME VIBRONIC BANDS IN THE $^3A_u \leftarrow {}^1A_g$ TRANSITION OF GLYOXAL. SPIN SPLITTINGS IN THE LOWEST TRIPLET STATE OF THE ISOLATED MOLECULE..15 min.(8:47)

L. H. SPANGLER, Los Alamos National Laboratory, MS-G738, Los Alamos, New Mexico, 87545; D. W. PRATT, Department of Chemistry University of Pittsburgh, Pittsburgh, Pennsylvania, 15260; and F. W. BIRSS, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2.

TC3. THE PHOSPHORESCENCE EXCITATION SPECTRUM OF JET COOLED BENZALDEHYDE..........15 min.(9:04)

K. W. HOLTZCLAW and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

TC4. PHOTOLUMINESCENCE STUDIES OF LAYERED TRANSITION METAL PHOSPHORUS CHALCOGENIDES AND THEIR PYRIDINE INTERCALATION COMPOUNDS....................15 min.(9:21)

D. A. CLEARY, E. LIFSHITZ, and A. H. FRANCIS, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

TC5. ANGULAR FACTORS IN THE MULTIPHOTON AND MULTIPOLE PHOTOFRAGMENTATION OF MOLECULES..15 min.(9:38)

YING-NAN CHIU, Center of Molecular Dynamics and Energy Transfer, Department of Chemistry, The Catholic University of America, Washington, D.C., 20064.

TC6. SPECTROSCOPIC INVESTIGATIONS OF SUPERSONICALLY COOLED BENZOIC ACID DIMER....15 min.(9:55)

MENG-CHIH SU and DAVID L. MONTS, Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas, 72701.

Intermission

TC7. ANOMALIES IN THE RYDBERG SPECTRUM OF 1,3-CYCLOPENTADIENE....................15 min.(10:30)

A. SABLJIĆ and R. McDIARMID, National Institutes of Health, Bethesda, Maryland, 20892. Permanent address of Sabljić: The Rudjer Bošković Institute, Zagreb, Yugoslavia.

TC8. THE SPECTROSCOPY OF UNSTABLE THIOCARBONYL COMPOUNDS.......................15 min.(10:47)

R. H. JUDGE and D. C. MOULE, Department of Chemistry, Brock University, St. Catharines, Ontario, Canada, L2S 3A1.

TC9. SPECTROSCOPY, LIFETIMES, AND QUENCHING OF THE METHOXY RADICAL...............15 min.(11:04)

NANCY L. GARLAND and DAVID R. CROSLEY, Molecular Physics Department, SRI International, Menlo Park, California, 94025.

TC10. THE TWO-PHOTON SPECTRUM OF THE S_1-S_0 TRANSITION IN GLYOXAL...................15 min.(11:21)

G. A. BICKEL and K. K. INNES, Department of Chemistry, State University of New York, University Center at Binghamton, Binghamton, New York, 13901.

TC11. Σ1 will be presented here (K. H. BOWEN)....................................15 min.(11:38)

TC12. Π2 will be presented here (R. K. YOO)......................................15 min.(11:55)

TUESDAY, JUNE 17, 1986 — 1:30 P.M.

Room 1153, Physics Laboratory

Chairman Before Intermission: W. E. BLASS, Department of Physics and Astronomy,
University of Tennessee, Knoxville, Tennessee.

Chairwoman After Intermission: CATHERINE M. DEELEY, Herzberg Institute of Astrophysics,
National Research Council of Canada, Ottawa, Ontario,
Canada.

TE1. INFRARED ROTATIONAL SPECTRUM OF $\tilde{X}\ ^3B_1$ CH_2 AROUND 400 cm^{-1}...................15 min.(1:30)

        T. J. SEARS, Department of Chemistry, Brookhaven National Laboratory,
Upton, New York, 11973.

TE2. DIODE LASER SPECTROSCOPY OF THE ν_2 BAND OF CH_2...............................15 min.(1:47)

        M. D. MARSHALL and A.R.W. McKELLAR, Herzberg Institute of Astrophysics,
National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

TE3. TIME-RESOLVED DIODE LASER SPECTROSCOPY OF THE CCH RADICAL PHOTOCHEMICALLY
GENERATED FROM ACETYLENE..10 min.(2:04)

        H. KANAMORI and E. HIROTA, Institute for Molecular Science, Okazaki 444,
Japan.

TE4. A NEW ASSIGNMENT OF THE NO_3 1490 cm^{-1} BAND TO AN ELECTRONIC TRANSITION......15 min.(2:16)

        K. KAWAGUCHI, E. HIROTA, Institute for Molecular Science, Okazaki 444,
Japan; T. ISHIWATA, and I. TANAKA, Department of Chemistry, Tokyo
Institute of Technology, Ohokayama, Meguro, Tokyo 152, Japan.

TE5. HIGH RESOLUTION SPECTROSCOPY OF FREE RADICALS USING A FOURIER TRANSFORM
SPECTROMETER...15 min.(2:33)

        P. D. HAMMER, J. B. BURKHOLDER, and C. J. HOWARD, Aeronomy Laboratory,
National Oceanic and Atmospheric Administration, 325 Broadway,
Boulder, Colorado, 80303.

TE6. THE FOURIER TRANSFORM INFRARED SPECTRUM OF CHCℓS..........................15 min.(2:50)

        CATHERINE M. DEELEY, Herzberg Institute of Astrophysics, National
Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

Intermission

TE7. GAS PHASE AND MATRIX ISOLATION SPECTRA AND FORCE FIELD OF 3H-DIAZIRINE......10 min.(3:25)

        B. P. WINNEWISSER, Physikalisch-Chemisches Institut, Justus Liebig
University Giessen, Heinrich-Buff-Ring 58, D-6300 Giessen, West Germany;
A. GAMBI, Dipartimento di Spettroscopia, Elettrochemica e Chimica
Fisica, Facolta di Chimica Industriale, Universita di Venezia, Calle
Larga S. Marta 2137, I-30123 Venice, Italy; and H. REISENAUER, Institut
für Organische Chemie, Justus Liebig University Giessen, Heinrich-Buff-
Ring 58, D-6300 Giessen, West Germany.

TE8. HIGH RESOLUTION MEASUREMENTS AND ANALYSIS OF THE ν_2, ν_3, ν_4, ν_5, AND $2\nu_9$
BANDS OF NITRIC ACID...15 min.(3:37)

        A. G. MAKI, W. B. OLSON, Molecular Spectroscopy Division, National
Bureau of Standards, Gaithersburg, Maryland, 20899; A. FAYT, Molecular
Spectroscopy Laboratory, Université de Louvain Chemin du Cyclotron, 2,
B-1348 Louvain-La-Neuve, Belgium; J. S. WELLS, Time and Frequency
Division, National Bureau of Standards, Boulder, Colorado, 80303; and
A. GOLDMAN, Department of Physics, University of Denver, Denver,
Colorado, 80208.

TE9. THE ABSORPTION SPECTRUM OF HNO_3 AROUND 7.2 μm...............................10 min.(3:54)

        O. LADO-BORDOWSKY, A. PERRIN, Laboratoire de Physique Moléculaire et
d'Optique Atmosphérique, CNRS, Campus d'Orsay, 91405 Orsay, France;
and A. VALENTIN, Laboratoire de Spectronomie Moléculaire, CNRS, Tour 13,
Université de Paris 6, 75230 Paris, France.

TE10. ABSORPTION OF $^{12}CH_3D$ AT 6-10 μm. FREQUENCIES AND INTENSITIES...............10 min.(4:06)

        G. TARRAGO, M. DELAVEAU, M. DANG-NHU, and G. GUELACHVILI, Laboratoire
d'Infrarouge, CNRS, Université de Paris-Sud, 91405 Orsay, France.

TE11. MEASUREMENT OF INTENSITIES, HYDROGEN- AND NITROGEN- BROADENED LINE
WIDTHS OF CH_3D AT LOW TEMPERATURES.......................................15 min.(4:18)

        SURYANARAYANAN CHUDAMANI and PRASAD VARANASI, Laboratory for Planetary
Atmospheres Research, State University of New York, Stony Brook,
New York, 11794-2300.

TE12. TUNABLE DIODE LASER MEASUREMENTS OF ABSOLUTE INTENSITIES AND LINEWIDTHS
IN THE ν_6 BAND OF $^{12}CH_3D$ NEAR 8.6 μm...10 min.(4:35)

K. B. THAKUR, Department of Physics, The Ohio State University,
Columbus, Ohio, 43210; V. MALATHY DEVI, Department of Physics, College
of William and Mary, Williamsburg, Virginia, 23185; C. P. RINSLAND,
and M.A.H. SMITH, Atmospheric Sciences Division, MS 401A, NASA/Langley
Research Center, Hampton, Virginia, 23665-5225.

TE13. ON THE ROTATIONAL RAMAN SPECTRUM OF CH_2D_2....................................15 min.(4:47)

W. F. MURPHY, Division of Chemistry, National Research Council of
Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

TUESDAY, JUNE 17, 1986 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chairman Before Intermission: H. S. GUTOWSKY, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois.

Chairman After Intermission: G. T. FRASER, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C.

TF1. THE ROTATIONAL SPECTRUM AND STRUCTURE OF CF_3H-NH_3..........................15 min.(1:30)

D. D. NELSON, JR., W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138; G. T. FRASER, F. J. LOVAS, and R. D. SUENRAM, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234.

TF2. VAN DER WAALS POTENTIALS FROM THE INFRARED SPECTRA OF RARE GAS-HF COMPLEXES.15 min.(1:47)

G. T. FRASER and A. S. PINE, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

TF3. ESTIMATES OF THE MOLECULAR QUADRUPOLE AND THE PARALLEL POLARIZABILITY OF BORON TRIFLUORIDE...10 min.(2:04)

STEWART NOVICK, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457.

TF4. PRODUCT STATE DISTRIBUTION OF THE PHOTODISSOCIATION OF THE $NeBr_2$ VAN DER WAALS MOLECULE..15 min.(2:16)

J. I. CLINE, III, D. D. EVARD, and K. C. JANDA, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

TF5. MOLECULAR BEAM-LASER SPECTROSCOPY OF THE $NeCl_2$ VAN DER WAALS MOLECULE.......15 min.(2:33)

D. D. EVARD, J. I. CLINE, III, K. C. JANDA, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260; and F. THOMMEN, CIBA-Geigy, Basel, Switzerland.

TF6. SUB-DOPPLER RESOLUTION INFRARED SPECTROSCOPY OF THE CARBON DIOXIDE DIMER....15 min.(2:50)

K. W. JUCKS, Z. S. HUANG, and R. E. MILLER, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27514.

TF7. LASER INDUCED FLUORESCENCE SPECTROSCOPY OF $C_6F_6^+ \cdot X_N$ WITH X = He, Ne, Ar, AND N_2...15 min.(3:07)

RICHARD KENNEDY, Department of Chemistry, Birmingham University, Birmingham, England; CHUNG-YI KUNG, and TERRY A. MILLER, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

Intermission

TF8. LASER EXCITATION SPECTRA FOR THE VINOXY-Ar RADICAL VAN DER WAALS COMPLEX...15 min.(3:40)

L. J. VAN DE BURGT, J. C. MALIEKAL, and M. C. HEAVEN, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, 60616.

TF9. INFRARED PHOTODISSOCIATION OF METHANE-ETHYLENE..............................15 min.(3:57)

S. R. HAIR and K. C. JANDA, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

TF10. ROTATIONAL SPECTRUM, INTERNAL ROTATION, AND STRUCTURE OF $Ar-CH_3Cl$............10 min.(4:14)

G. T. FRASER, R. D. SUENRAM, and F. J. LOVAS, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

TF11. METHANOL CLUSTERS OF TRYPTOPHAN ANALOGUES BY PHOTOIONIZATION SPECTROSCOPY...15 min.(4:26)

L. A. PETEANU, Y. D. PARK, and D. H. LEVY, Department of Chemistry and The James Franck Institute, University of Chicago, Chicago, Illinois, 60637.

TF12. ROTATIONAL SPECTRA AND STRUCTURE OF DIBORANE-HYDROGEN HALIDE DIMERS.........15 min.(4:43)

H. S. GUTOWSKY, T. EMILSSON, J. D. KEEN, T. D. KLOTS, and C. CHUANG, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.

TF13. ROTATIONAL SPECTRA AND STRUCTURE OF THE HCN TRIMER.........................15 min.(5:00)

R. S. RUOFF, T. EMILSSON, T. D. KLOTS, C. CHUANG, and H. S. GUTOWSKY, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinoiw, 61801.

TF14. $\Sigma4$ will be presented here (D. D. NELSON)...................................10 min.(5:12)

TF15. $\Sigma5$ will be presented here (D. J. YARON)....................................10 min.(5:24)

TUESDAY, JUNE 17, 1986 — 1:30 P.M.

Room 1005, Physics Laboratory

Chairman Before Intermission: P. MISRA, Department of Physics, The Ohio State University, Columbus, Ohio.

Chairwoman After Intermission: B. SWEETING, Department of Chemistry, The Ohio State University, Columbus, Ohio.

TG1.   LASER INDUCED FLUORESCENCE OF THE Rb_2 MOLECULE..............................10 min.(1:30)

C. AMIOT, Laboratoire de Physique Moléculaire et Optique Atmosphérique, CNRS, Campus d'Orsay, 91405 Orsay, France; and J. VERGES, Laboratoire Aimé Cotton, Campus d'Orsay, 91405 Orsay, France.

TG2.   PERTURBATION ANALYSIS IN THE ASUNDI SYSTEM $(a'^3\Sigma^+ \rightarrow a^3\Pi)$ OF $^{13}C^{16}O$ AND IN THE BALLIK-RAMSAY SYSTEM $(b^3\Sigma^- \rightarrow a^3\Pi)$ OF $^{13}C_2$, $^{12}C^{13}C$...............10 min.(1:42)

C. AMIOT and K. ISLAMI, Laboratoire de Physique Moléculaire et Optique Atmosphérique, CNRS, Campus d'Orsay, 91405 Orsay, France.

TG3.   THE OPTICAL SPECTRUM OF NIOBIUM MONOXIDE, NbO...............................15 min.(1:54)

A. G. ADAM, Y. AZUMA, J. A. BARRY, A. J. MERER, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Y6; G. CHEVAL, J. L. FEMENIAS, Laboratoire d'Optique Atomique et Moléculaire, Université de Nice, Nice 06034, France; and U. SASSENBERG, Department of Physics, University of Stockholm, S-113 46 Stockholm, Sweden.

TG4.   LASER SPECTROSCOPY AND STRUCTURE OF MgOH: VIBRATIONAL AND ROTATIONAL ANALYSIS..15 min.(2:11)

YONG NI and DAVID O. HARRIS, Department of Chemistry and Quantum Institute, University of California, Santa Barbara, California, 93106.

TG5.   LASER SPECTROSCOPY AND STRUCTURE OF MgOH: SPIN-ROTATION INTERACTION........10 min.(2:28)

YONG NI and DAVID O. HARRIS, Department of Chemistry and Quantum Institute, University of California, Santa Barbara, California, 93106.

TG6.   LASER-MICROWAVE DOUBLE RESONANCE LASER SPECTROSCOPY OF ALKALINE EARTH MONOHALIDES: HYPERFINE STRUCTURE AND ELECTRIC DIPOLE MOMENTS IN GROUND AND EXCITED STATES.......................Specially Arranged..................25 min.(2:40)

W. E. ERNST, Department of Chemistry, Stanford University, Stanford, California, 94305

Intermission

TG7.   OPTICAL-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF SrF: ANALYSIS OF THE HIGH-LYING $F^2\Sigma^+$ - AND $G^2\Pi$-STATES...15 min.(3:25)

J. O. SCHRÖDER, C. NITSCH, and W. E. ERNST, Institut für Molekülphysik, Freie Universität Berlin, D-1000 Berlin 33, Germany.

TG8.   THE LAMBDA DOUBLING SPECTRUM OF ^{13}CH, STUDIED BY MICROWAVE-OPTICAL DOUBLE RESONANCE..10 min.(3:42)

T. C. STEIMLE, Department of Chemistry, Arizona State University, Tempe, Arizona, 85287; D. R. WOODWARD, and J. M. BROWN, Physical Chemistry Laboratory, Oxford University, Oxford, England, OX1 3QZ.

TG9.   LASER-INDUCED FLUORESCENCE OF HCO RADICAL....................................15 min.(3:54)

BRADLEY M. STONE, Department of Chemistry, San Jose State University, San Jose, California, 95192; MARCUS NOBLE, Department of Chemistry, University of Southern California, Los Angeles, California, 90007; and EDWARD K.C. LEE, Department of Chemistry, University of California, Irvine, California, 92717.

TG10.   CHEMILUMINESCENT REACTIONS OF MOLECULAR FLUORINE WITH ORGANOSULFUR COMPOUNDS..10 min.(4:11)

R. J. GLINSKI, E. A. MISHALANIE, National Center for Atmospheric Research, PO Box 3000, Boulder, Colorado, 80307; and J. W. BIRKS, Department of Chemistry and CIRES, University of Colorado, Boulder, Colorado, 80309.

TG11.   ELECTRONIC SPECTRA OF THIOFORMALDEHYDE, SELENOFORMALDEHYDE, AND OTHER SMALL MOLECULES BY CHEMILUMINESCENCE..15 min.(4:23)

R. J. GLINSKI, National Center for Atmospheric Research, PO Box 3000, Boulder, Colorado, 80307; and J. W. BIRKS, Department of Chemistry and CIRES, University of Colorado, Boulder, Colorado, 80309.

TG12.   QUANTUM BEAT AND ANTICROSSING SPECTROSCOPY OF ACETYLENE WITH 45 000 cm^{-1}
        OF ENERGY: IMPLICATIONS IN INTERNAL CONVERSION AND INTERSYSTEM CROSSING....15 min.(4:40)

P. G. GREEN, R. W. FIELD, J. L. KINSEY, E. ABRAMSON, N. SHAH,
Department of Chemistry, and G. Harrison Spectroscopy Laboratory,
Massachusetts Institute of Technology, Cambridge, Massachusetts,
02139; M. LOMBARDI, P. DUPRE, and R. JOST, Service National des
Champs Intenses, CNRS, 38042 Grenoble, France.

WEDNESDAY, JUNE 18, 1986 -- 8:45 A.M.

Auditorium, Independence Hall

Chairman: K. NARAHARI RAO, Department of Physics,
           The Ohio State University, Columbus, Ohio.

Plenary Session

WA1. RYDBERG TRANSITIONS AND RYDBERG MOLECULES................40 min.

>   G. HERZBERG, Herzberg Institute of Astrophysics,
      National Research Council of Canada, Ottawa,
      Ontario, Canada, K1A OR6.

WA2. SPECTROSCOPY OF MOLECULAR IONS AT THEIR DISSOCIATION
      LIMITS...40 min.

>   ALAN CARRINGTON, Physical Chemistry Laboratory,
      Oxford University, South Parks Road, Oxford,
      England, OX1 3QZ.

Intermission

WA3. DYNAMICS OF SUB-DOPPLER RESOLVED STATES IN THE
      CHANNEL 3 REGION OF BENZENE..............................40 min.

>   E. W. SCHLAG, Institut für Physikalische und
      Theoretische Chemie der Technischen Universität
      München, D-8046 Garching, West Germany.

WEDNESDAY, JUNE 18, 1986 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chairman: TAKESHI OKA, Department of Chemistry and
           Department of Astronomy and Astrophysics,
           The University of Chicago, Chicago, Illinois.

Plenary Session

WE1. FUNDAMENTAL AND OVERTONE ROTATION-VIBRATION
      SPECTRUM OF HT...40 min.

>   RICHARD N. ZARE, Department of Chemistry,
      Stanford University, Stanford, California 94305.

WEDNESDAY, JUNE 18, 1986 — 2:30 P.M.

Room 1153, Physics Laboratory

Chairman: R. J. JAKOBSEN, Mattson Institute for Spectroscopic Research, Columbus, Ohio.

WE'1. VIBRATIONAL ANALYSIS OF THE OVERTONE SPECTRA OF CHLOROTRIFLUOROMETHANE......10 min.(2:30)

      A. M. DE SOUZA and D. S. PERRY, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

WE'2. VIBRATIONAL SPECTRA OF 3-CHLOROCYCLOPROPENE AND ITS DEUTERIUM ISOTOPOMERS; A POTENTIAL FUNCTION FOR THIS MOLECULAR SYSTEM............................15 min.(2:42)

      NORMAN C. CRAIG, JULIANTO PRANATA, JULIAN R. SPRAGUE, SARA JAMIE REINGANUM, and PHILIP S. STEVENS, Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074.

WE'3. VIBRATIONAL SPECTRA OF 3-FLUOROCYCLOPROPENE AND 3-FLUOROCYCLOPROPENE-$\underline{d}_3$.....10 min.(2:59)

      NORMAN C. CRAIG, JULIANTO PRANATA, JULIAN R. SPRAGUE, and PHILIP S. STEVENS, Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074.

WE'4. THE VIBRATIONAL SPECTRA AND HARMONIC AB INITIO FORCE FIELDS FOR BICYCLO [2.2.1] HEPTANE AND SEVERAL ANALOGS.................................15 min.(3:11)

      C. CASTRO, R. DUTLER, A. RAUK, R. A. SHAW, and H. WIESER, Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, T2N 1N4.

WE'5. THE VAPOUR PHASE INFRARED SPECTRA IN THE REGION OF 700-100 cm^{-1} OF BICYCLO[3.2.1]OCTANE AND ITS 8-OXA, 6-OXA, 6-OXA-7,7-D_2, AND 6,8-DIOXA ANALOGS: EVIDENCE FOR ANHARMONIC SKELETAL DEFORMATIONS.....................10 min.(3:28)

      C. CASTRO, N. IBRAHIM, A. RAUK, R. A. SHAW, H. WIESER, Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, T2N 1N4; and T. L. SMITHSON, DREV, 2459 Blvd. Pie XI NORD, C.P. 8800, Courcelette, Quebec, Canada, GOA 1RO.

WE'6. INTERNAL HYDROGEN BONDING IN CYCLIC AMIDES.................................15 min.(3:40)

      D. P. McDERMOTT and V. A. MEIER, Department of Chemistry, Lafayette College, Easton, Pennsylvania, 18042.

WE'7. ON THE NATURE OF HIGH CF_4 VIBRATIONAL LEVELS EXCITED BY PROTON ENERGY LOSS SPECTROSCOPY..15 min.(3:57)

      HAROLD B. LEVENE, Department of Chemistry, University of California, Irvine, California, 92717; and DAVID S. PERRY, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

WEDNESDAY, JUNE 18, 1986 -- 2:30 P.M.

Room 1009, Physics Laboratory

Chairman: J.K.G. WATSON, Herzberg Institute of Astrophysics, National Research Council
of Canada, Ottawa, Ontario, Canada.

WF1.   ANALYSIS OF THE Q-BRANCH REGION OF THE $3\nu_3$ OVERTONE OF UF_6: THE IMPLIED
STRUCTURE OF THE $n\nu_3$ LADDER...15 min.(2:30)

B. J. KROHN, R. S. McDOWELL, C. W. PATTERSON, N. G. NERESON, and
M. J. REISFELD, Los Alamos National Laboratory, University of
California, Los Alamos, New Mexico, 87545.

WF2.   INFRARED SPECTRA OF TeF_6. ISOTOPE SHIFTS AND FORCE CONSTANTS IN
HEXAFLUORIDE MOLECULES...15 min.(2:47)

R. S. McDOWELL, R. F. HOLLAND, W. H. McCULLA, G. K. ANDERSON, and
M. J. REISFELD, Los Alamos National Laboratory, University of
California, Los Alamos, New Mexico, 87545.

WF3.   FAR-INFRARED SPECTRUM OF METHYLAMINE AND THE GROUP THEORETICAL TREATMENT
OF ITS LARGE AMPLITUDE MOTIONS..15 min.(3:04)

N. OHASHI, Department of Physics, Faculty of Science, Kanazawa
University, Kanazawa 920, Japan; K. TAKAGI, Department of Physics,
Frculty of Science, Toyama University, Toyama 930, Japan;
W. J. LAFFERTY, W. B. OLSON, and J. T. HOUGEN, Molecular Spectroscopy
Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

WF4.   THE NONRIGID BENDER HAMILTONIAN MARK TWO....................................15 min.(3:21)

R. BEARDSWORTH, Digital Equipment GmbH, 8000 Munich 45, West Germany;
P. R. BUNKER, Herzberg Institute of Astrophysics, National Research
Council of Canada, Ottawa, Ontario, Canada, K1A OR6; PER JENSEN,
Department of Chemistry, University of Aarhus, Aarhus, Denmark; and
W. P. KRAEMER, Max-Planck Institute for Astrophysics, Garching,
West Germany.

WF5.   LOCAL MODE THEORY: ANHARMONIC DEGENERATE OSCILLATORS.......................15 min.(3:38)

F. MICHELOT and J. MORET-BAILLY, Laboratoire de Spectronomie Moléculaire
et Instrumentation Laser, CNRS, Université de Bourgogne, 21100 Dijon,
France.

WF6.   NEW INTERPRETATION OF THE ROTATIONAL QUANTUM NUMBER R FOR TRIPLY
DEGENERATE FUNDAMENTALS OF SPHERICAL-TOP MOLECULES..........................15 min.(3:55)

GRIGORY A. NATANSON, Department of Chemistry, Northwestern University,
Evanston, Illinois, 60201.

WEDNESDAY, JUNE 18, 1986 — 2:30 P.M.

Room 1005, Physics Laboratory

Chairman: R. J. SAYKALLY, Department of Chemistry, University of California,
            Berkeley, California.

WG1.   HIGH RESOLUTION, CW LASER INDUCED CHARGE TRANSFER STUDY OF CO^+ AND N_2^+.......10 min.(2:30)

       C.-H. KUO, Department of Chemistry, University of California,
       Santa Barbara, California, 93106; I. MILKMAN, Y. AL-RAMADIN,
       J. T. MOSELEY, Department of Physics, University of Oregon,
       Eugene, Oregon, 97403; and T. C. STEIMLE, Department of Chemistry,
       Arizona State University, Tempe, Arizona, 85287.

WG2.   INFRARED SPECTROSCOPY OF THE $A^2\Pi_u - X^2\Sigma_g^+$ ELECTRONIC TRANSITIONS OF C_2^-.......15 min.(2:42)

       B. D. REHFUSS, D.-J. LIU, B. M. DINELLI, M.-F. JAGOD, M. W. CROFTON,
       and T. OKA, Department of Chemistry and Department of Astronomy and
       Astrophysics, The University of Chicago, Chicago, Illinois, 60637.
       Permanent address of Dinelli: Istituto di Spettroscopia Molecolare
       del C.N.R., Bologna, Italy.

WG3.   HIGH RESOLUTION LASER SPECTROSCOPY OF $SrOCH_3$...............................15 min.(2:59)

       L. C. ELLINGBOE, C. R. BRAZIER and P. F. BERNATH, Department of
       Chemistry, University of Arizona, Tucson, Arizona, 85721.

WG4.   THE $\tilde{A} \leftarrow \tilde{X}$ SYSTEMS OF THE ALKYL-O AND ALKYL-S RADICALS......................15 min.(3:16)

       CRISTINO P. DAMO, STEPHEN C. FOSTER, YEN-CHU HSU, XIANMING LIU,
       CHUNG-YI KUNG, and TERRY A. MILLER, Department of Chemistry,
       The Ohio State University, Columbus, Ohio, 43210.

WG5.   LASER SPECTROSCOPY OF ISO-PROPOXY AND ETHOXY FREE RADICALS..................15 min.(3:33)

       XIANMING LIU, CRISTINO DAMO, STEPHEN C. FOSTER, CHUNG-YI KUNG,
       YEN-CHU HSU, and TERRY A. MILLER, Department of Chemistry,
       The Ohio State University, Columbus, Ohio, 43210.

WG6.   PROMINENT, AND RESTRICTED, VIBRATIONAL STATE MIXING IN THE FLUORESCENCE
       EXCITATION SPECTRUM OF BENZOPHENONE.......................................15 min.(3:50)

       K. W. HOLTZCLAW and D. W. PRATT, Department of Chemistry, University
       of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

PLEASE NOTE:

    AT 4:30 P.M., WE WILL HAVE A DEDICATION OF THE LASER SPECTROSCOPY FACILITY
ACCOMPANIED BY A RECEPTION (WITH REFRESHMENTS) IN THE FACILITY BETWEEN
5:30 AND 6:45. THIS IS FOLLOWED BY THE TRADITIONAL SOCIAL HOUR AT THE FACULTY
CLUB WITH THE BANQUET AT 7:30. WE HOPE YOU WILL JOIN US FOR THESE EVENTS.

THURSDAY, JUNE 19, 1986 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chairman: R. J. BARTLETT, Quantum Theory Project, University of Florida,
            Gainesville, Florida.

RA1.   THEORETICAL STUDY OF POTENTIAL ENERGY SURFACES OF EXCITED ELECTRONIC
       STATES OF SMALL MOLECULAR SYSTEMS..................Invited Paper............40 min.(8:30)

            KEIJI MOROKUMA, Department of Chemistry, Institute for Molecular Science,
            Myodaiji, Okazaki 444, Japan.

RA2.   AB INITIO CALCULATIONS OF POTENTIAL ENERGY CURVES AND TRANSITION
       MOMENTS FOR $^1\Sigma_u^+$ STATES OF N_2..15 min.(9:15)

            WALTER C. ERMLER, JOSEPH P. CLARK, Department of Chemistry and
            Chemical Engineering, Stevens Institute of Technology, Hoboken,
            New Jersey, 07030; and ROBERT S. MULLIKEN, Department of Chemistry,
            University of Chicago, Chicago, Illinois, 60637.
            Happy 90th Birthday Professor Mulliken!

RA3.   THEORETICAL STUDY OF THE ELECTRIC DIPOLE MOMENT FUNCTION OF THE
       ClO MOLECULE...15 min.(9:32)

            L.G.M. PETTERSSON, S. R. LANGHOFF, NASA/Ames Research Center, Moffett
            Field, California, 94035; and D. P. CHONG, Department of Chemistry,
            University of British Columbia, Vancouver, British Columbia, Canada,
            V6T 1Y6.

RA4.   ESTIMATION OF VIBRATIONAL-ROTATIONAL TRANSITION INTENSITIES FROM THE
       VIBRATIONAL DEPENDENCE OF THE DIPOLE MOMENT: OH AND ClO....................15 min.(9:49)

            D. J. YARON, K. I. PETERSON, and W. KLEMPERER, Department of Chemistry,
            Harvard University, Cambridge, Massachusetts, 02138.

RA5.   SPIN-ORBIT SPLITTING IN FIRST, SECOND, AND THIRD TRANSITION ROW METALS......15 min.(10:06)

            R. B. ROSS and W. C. ERMLER, Department of Chemistry and Chemical
            Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

Intermission

RA6.   ELECTRONIC STRUCTURE OF HEAVY-ATOM MOLECULES...............................15 min.(10:40)

            RUSSELL M. PITZER, Department of Chemistry, The Ohio State University,
            Columbus, Ohio, 43210; and NICHOLAS W. WINTER, Lawrence Livermore
            National Laboratory, MS L487, PO Box 5508, Livermore, California, 94550.

RA7.   PHOTOIONIZATION CROSS SECTIONS FOR CO_2 BY THE COMPLEX BASIS FUNCTION
       METHOD..15 min.(10:57)

            CHIN-HUI YU and C. WILLIAM McCURDY, Department of Chemistry, The Ohio
            State University, Columbus, Ohio, 43210.

RA8.   USING ENERGY DERIVATIVES TO FIND STATIONARY POINTS ON POTENTIAL ENERGY
       SURFACES..15 min.(11:14)

            DONALD C. COMEAU, ROBERT J. ZELLMER, and ISAIAH SHAVITT, Department
            of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

RA9.   AB INITIO VIBRATIONAL TRANSITION DIPOLE MOMENTS AND BAND INTENSITIES
       OF FORMALDEHYDE...15 min.(11:31)

            H. C. HSIEH and W. C. ERMLER, Department of Chemistry and Chemical
            Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

RA10. CENTRIFUGAL DISTORTIONS IN MOLECULES: AN AB INITIO APPROACH................15 min.(11:48)

            L. L. LOHR and J.-M.J. POPA, Department of Chemistry, University of
            Michigan, Ann Arbor, Michigan, 48109.

THURSDAY, JUNE 19, 1986 — 8:30 A.M.

Room 1009, Physics Laboratory

Chairman Before Intermission: W. H. WEBER, Department of Physics, Research Staff, Ford Motor Company, Dearborn, Michigan.

Chairman After Intermission: G. A. NATANSON, Department of Chemistry, Northwestern University, Evanston, Illinois.

RB1. SATURATION STARK SPECTROSCOPY AND GLOBAL ANALYSIS OF THE PRINCIPAL ISOTOPIC SPECIES OF OCS..10 min. (8:30)

> J-G LAHAYE, R. VANDENHAUTE, and A. FAYT, Molecular Spectroscopy Laboratory, Catholic University of Louvain, 2 Chemin du Cyclotron - B-1348, Louvain-la-Neuve, Belgium.

RB2. THE CARBON DIOXIDE MOLECULE: A TEST CASE FOR THE r_o, r_e AND r_m STRUCTURES..10 min. (8:42)

> G. GRANER, C. ROSSETTI, and D. BAILLY, Laboratoire d'Infrarouge, CNRS, Université de Paris-Sud, 91405 Orsay, France.

RB3. FLUOROFORM: A NEW ANALYSIS OF THE POLYAD AT 8-9 MICRONS....................10 min. (8:54)

> G. GRANER, Laboratoire d'Infrarouge, CNRS, Université de Paris-Sud, 91405 Orsay, France; and J. P. CHAMPION, Laboratoire de Spectronomie Moléculaire et Instrumentation Laser, Université de Dijon, 21100 Dijon, France.

RB4. EXPERIMENTAL VALUES FOR THE ROTATIONAL CONSTANTS OF THE OG AND 1G TORSIONAL COMPONENTS OF THE VIBRATIONAL GROUND STATE OF H_2O_2, AND THE MATRIX ELEMENT COUPLING THEM...20 min. (9:06)

> W. B. OLSON, A. G. MAKI, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899; R. H. HUNT, Department of Physics, Florida State University, Tallahassee, Florida, 32306; J. W. BRAULT, Kitt Peak National Laboratory, 950 North Cherry Avenue, PO Box 26732, Tucson, Arizona, 85726; and L. R. BROWN, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, California, 91109.

RB5. THE STATE OF THE ANALYSIS OF $\nu_9 + \nu_4 - \nu_4$ OF ETHANE.............................15 min. (9:28)

> W. E. BLASS, Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee, 37996-1200; G. W. HALSEY, D. E. JENNINGS, D. REUTER, and J. SUSSKIND, Planetary Systems Branch, Code 693.2, NASA/Goddard Space Flight Center, Greenbelt, Maryland, 20771.

RB6. FIRST STRATOSPHERIC MEASUREMENTS OF CARBONYL FLUORIDE (COF_2) FROM HIGH RESOLUTION INFRARED SOLAR ABSORPTION SPECTRA OBTAINED BY THE ATMOS EXPERIMENT ABOARD SPACELAB 3..10 min. (9:45)

> C. P. RINSLAND, J. H. PARK, J. M. RUSSELL III, NASA/Langley Research Center, MS 401A, Hampton, Virginia, 23665-5225; R. ZANDER, Institute of Astrophysics, University of Liege, Liege-Ougree, Belgium; L. R. BROWN, C. B. FARMER, and R. A. NORTON, Jet Propulsion Laboratory, MS 183-301, 4800 Oak Grove Drive, Pasadena, California, 91109.

RB7. THE HIGH RESOLUTION SPECTRUM AND ROTATIONAL ANALYSIS OF THE ν_6 BAND OF CARBONYL FLUORIDE...10 min. (9:57)

> K. B. THAKUR, K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio, 43210; R. R. FRIEDL, Jet Propulsion Laboratory, MS 183-601, 4800 Oak Grove Drive, Pasadena, California, 91109; C. P. RINSLAND, NASA/Langley Research Center, MS 401A, Hampton, Virginia, 23665-5225; and V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185.

RB8. THE FAR-INFRARED TORSIONAL SPECTRUM OF METHYL SILANE: FREQUENCY AND INTENSITY ANALYSIS..15 min. (10:09)

> N. M. MOAZZEN-AHMADI, H. JAGANNATH, and I. OZIER, Department of Physics, University of British Columbia, Vancouver, British Columbia, Canada, V6T 2A6. Present address of Jagannath: Department of Physics, Alabama A & M University, Normal, Alabama, 35762.

Intermission

RB9.   LASER-STARK AND FOURIER TRANSFORM SPECTRA OF THE ν_3 BAND OF FORMIC ACID....15 min.(10:40)

W. H. WEBER, P. D. MAKER, Department of Physics, Research Staff, Ford
Motor Company, Dearborn, Michigan, 48121; and J.W.C. JOHNS, Herzberg
Institute of Astrophysics, National Research Council of Canada, Ottawa,
Ontario, Canada, K1A OR6.

RB10. ANALYSIS OF THE COLLISION INDUCED FAR IR SPECTRUM OF CYCLOPROPANE...........10 min.(10:57)

W. R. GRONLUND, Chemistry Section (ds-1), Department of Science,
United States Coast Guard Academy, New London, Connecticut, 06320;
R. C. COHEN, Department of Chemistry, University of California-Berkeley,
Berkeley, California, 94720; and W. C. PRINGLE, Department of Chemistry,
Hall-Atwater Laboratories, Wesleyan University, Middletown, Connecticut,
06457.

RB11. INFRARED-INFRARED DOUBLE RESONANCE IN CH_3F AND NH_3.........................15 min.(11:09)

SANG K. LEE and R. H. SCHWENDEMAN, Department of Chemistry, Michigan
State University, East Lansing, Michigan, 48824.

RB12. INFRARED RADIO DOUBLE RESONANCE SPECTROSCOPY OF CF_3Br......................15 min.(11:26)

WAFAA FAWZY and R. H. SCHWENDEMAN, Department of Chemistry, Michigan
State University, East Lansing, Michigan, 48824.

RB13. LINESHAPES OF INFRARED RADIOFREQUENCY DOUBLE RESONANCE SPECTRA IN CH_3I......15 min.(11:43)

WAFAA FAWZY and R. H. SCHWENDEMAN, Department of Chemistry, Michigan
State University, East Lansing, Michigan, 48824.

THURSDAY, JUNE 19, 1986 — 8:30 A.M.

Room 1005, Physics Laboratory

Chairman: V. F. KALASINSKY, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi.

RC1.   VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF FOUR DISTINCT CONFORMATIONAL STATES OF POLY(L-LYSINE) IN AQUEOUS SOLUTION...............................15 min.(8:30)

       M. G. PATERLINI, T. B. FREEDMAN, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13244-1200.

RC2.   VIBRATIONAL CIRCULAR DICHROISM OF TARTARIC ACID ESTERS. CONFIGURATIONAL CORRELATION AND UNIQUE SENSITIVITY TO HYDROGEN BONDING EFFECTS...............15 min.(8:47)

       T. CHANDRAMOULY, C. S. EWIG, and P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

RC3.   THE VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF 2-METHYLOXETAN AND 3-METHYLOXETAN-2,2-D_2...15 min.(9:04)

       R. A. SHAW, N. IBRAHIM, and H. WIESER, Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, T2N 1N4.

RC4.   VIBRATIONAL CIRCULAR DICHROISM OF AMINO ACIDS AND OLIGOPEPTIDES AS A FUNCTION OF SOLUTION pH..15 min.(9:21)

       W. M. ZUK, A. N. SCANGAS, T. B. FREEDMAN, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13244.

RC5.   BOND-POLARIZABILITY RAMAN OPTICAL ACTIVITY CALCULATIONS OF (S)-(-)- EPOXYPROPANE AND COMPARISON TO EXPERIMENT.....................................10 min.(9:38)

       JUAN R. ESCRIBANO, Department of Chemistry, Syracuse University, Syracuse, New York, 13244-1200; and LAURENCE D. BARRON, Department of Chemistry, The University, Glasgow, United Kingdom, G12 8QQ.

RC6.   FOURIER TRANSFORM INFRARED VIBRATIONAL CIRCULAR DICHROISM OF MATRIX ISOLATED MOLECULES...10 min.(9:50)

       D. O. HENDERSON and P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

Intermission

RC7.   VIBRATIONAL CIRCULAR DICHROISM IN TRANSITION METAL COMPLEXES. RING CONFORMATION AND RING CURRENTS..15 min.(10:15)

       T. B. FREEDMAN, D. A. YOUNG, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13244-1200.

RC8.   A LOCAL MODE THEORY FOR VIBRATIONAL ABSORPTION AND CIRCULAR DICHROISM.......15 min.(10:32)

       P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

RC9.   VIBRATIONAL CIRCULAR DICHROISM AS A CRITERION FOR LOCAL MODE VERSUS NORMAL MODE BEHAVIOR..15 min.(10:49)

       S. ABBATE, Istituto di Chimica delle Macromolecole, C.N.R., Milano, Italy; G. LONGHI, Dipartimento di Chimica Industriale, Politecnico, Milano, Italy; L. RICHARD, Laboratoire de Spectroscopie Infrarouge, Bordeaux, France; C. BERTUCCI, C. ROSINI, P. SALVADORI, Centro Studi C.N.R. delle Molecole Stereoordinate e Otticamente Attive, Pisa, Italy; and A. MOSCOWITZ, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455.

RC10.   ROTATIONAL OPTICAL ACTIVITY..15 min.(11:06)

       P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

RC11.   VIBRATIONAL ABSORPTION AND CIRCULAR DICHROISM STUDIES ON CARBOHYDRATES......15 min.(11:23)

       D. M. BACK and P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

RC12.   Π3 will be presented here (GUNTER GEORG HOFFMANN)..........................10 min.(11:40)

RC13.   Π1 will be presented here (T. A. KEIDERLING)................................10 min.(11:52)

THURSDAY, JUNE 16, 1986 — 8:30 A.M.

Room 1008, Evans Chemical Laboratory

Chairman: BERNARD FRIDOVICH, Vice President, Research & Development,
Research & Data Systems, Inc., Lanham, Maryland 20706.

RD1. MILLIMETER WAVE SPECTRUM OF THE NS FREE RADICAL IN ITS FIRST SIX
VIBRATIONAL STATES..10 min.(8:30)

J. ANACONA, P. B. DAVIES, Department of Physical Chemistry, University
of Cambridge, Cambridge CB2 1EP, United Kingdom; M. BOGEY, C. DEMUYNCK, and
J. L. DESTOMBES, Université de Lille, Laboratoire de Spectroscopie
Hertzienne, CNRS, F 59655 Villeneuve d'Ascq, France.

RD2. MICROWAVE STUDIES OF SMALL CLUSTERS IN THE Ar/HF SYSTEM.....................15 min.(8:42)

C. CHUANG, T. D. KLOTS, T. EMILSSON, and H. S. GUTOWSKY, Noyes
Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.

RD3. ROTATIONAL SPECTRA AND STRUCTURES OF SMALL CLUSTERS: Ar_2-HCl AND Ar_3-HCl....15 min.(8:59)

T. D. KLOTS, R. S. RUOFF, C. CHUANG, and H. S. GUTOWSKY, Noyes
Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.

RD4. ROTATIONAL SPECTROSCOPY OF SMALL CLUSTERS WITH A FLYGARE FOURIER TRANSFORM
MICROWAVE SPECTROMETER...15 min.(9:16)

T. EMILSSON and H. S. GUTOWSKY, Noyes Chemical Laboratory, University
of Illinois, Urbana, Illinois, 61801.

RD5. MICROWAVE AND MICROWAVE-MICROWAVE DOUBLE RESONANCE SPECTROSCOPY OF
TORSIONALLY EXCITED METHYL FORMATE...15 min.(9:33)

GRANT M. PLUMMER, I. Physikalisches Institut, Universität zu Köln,
Zülpicher Strasse 77, 5000 Köln 41, Federal Republic of Germany;
ADAM WALTERS, and JOHN G. BAKER, Schuster Laboratory, University
of Manchester, Manchester M13 9PL, England.

RD6. DIRECT OBSERVATION OF TORSIONAL LEVELS AND VIBRATION-TORSION-ROTATION
INTERACTION IN RAMAN SPECTRA OF C_2H_6......................................15 min.(9:50)

R. FANTONI, K. VAN HELVOORT, W. KNIPPERS, J. REUSS, and W. L. MEERTS,
Fysisch Laboratorium, Katholieke Universiteit Nijmegen, Toernooiveld,
6525 ED Nijmegen, The Netherlands. Permanent address of Fantoni:
Lab. Spettroscopia Moleculare ENEA, CRE Frascati, Italy.

THURSDAY, JUNE 16, 1986 — 10:15 A.M.

Room 1008, Evans Chemical Laboratory

Chairman: YING-NAN CHIU, Center of Molecular Dynamics and Energy Transfer, Department
of Chemistry, The Catholic University of America, Washington, D.C.

RD'1. OBSERVATION OF CALCIUM AND STRONTIUM MONOALKYLAMIDES AND A
ROTATIONAL ANALYSIS OF SrNH$_2$...15 min.(10:15)

C. R. BRAZIER, A.M.R.P. BOPEGEDERA, and P. F. BERNATH, Department of
Chemistry, University of Arizona, Tucson, Arizona, 85721.

RD'2. ORGANOMETALLIC FREE RADICALS: OBSERVATION OF OPEN-FACED SANDWICH COMPLEXES
OF ALKALINE EARTH METALS...15 min.(10:32)

L. ELLINGBOE, C. BRAZIER, D. BOPEGEDERA, and P. BERNATH, Department of
Chemistry, University of Arizona, Tucson, Arizona, 85721.

RD'3. LIFETIME MEASUREMENTS OF THE INDIVIDUAL MOLECULAR EIGENSTATES OF THE
PERTURBED J'=0 LEVELS OF THE ^{1}B$_{3u}$ STATE OF PYRAZINE.......................15 min.(10:49)

W. M. VAN HERPEN, W. L. MEERTS, Fysisch Laboratorium, Katholieke
Universiteit Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands;
K. E. DRABE, Physical Chemical Laboratory, V. U. Amsterdam,
de Boelelaan 1081, 1081 HV Amsterdam, The Netherlands; and
J. KOMMANDEUR, Laboratory for Physical Chemistry, University of
Groningen, Nijenborgh 16, 9747 AC Groningen, The Netherlands.

RD'4. THE OPTICAL SPECTRUM OF NO$_2$: SPECTRAL ERGODICITY WITHOUT LEVEL REPULSION...15 min.(11:06)

KEVIN K. LEHMANN, Department of Chemistry, Princeton University,
Princeton, New Jersey, 08544; STEPHEN L. COY, Department of Chemistry,
Harvard University, Cambridge, Massachusetts, 02138; and JOHN P. PIQUE,
Department of Chemistry, Massachusetts Institute of Technology, Cambridge,
Massachusetts, 02139.

RD'5. THE FLUORESCENCE AND PHOSPHORESCENCE EXCITATION SPECTRA OF JET COOLED
ACETOPHENONE...15 min.(11:23)

J. L. TOMER, K. W. HOLTZCLAW, D. W. PRATT, Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania, 15260; and
L. H. SPANGLER, Los Alamos National Laboratory, MS-G738, Los Alamos,
New Mexico, 87545.

RD'6. ROTATIONALLY RESOLVED FLUORESCENCE EXCITATION SPECTRUM OF STILBENE..........15 min.(11:40)

W. M. VAN HERPEN, W. L. MEERTS, Fysisch Laboratorium, Katholieke
Universiteit Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands;
M. V. RAMAKRISHNA, and D. W. PRATT, Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

THURSDAY, JUNE 19, 1986 — 1:30 P.M.

Room 1153, Physics Laboratory

Chairman: T. AMANO, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada.

RE1. HYDROGEN MIGRATION TUNNELING EFFECTS IN THE INFRARED SPECTRUM OF PROTONATED ACETYLENE $C_2H_3^+$...15 min.(1:30)

    JON HOUGEN, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RE2. ROTATION-VIBRATION ENERGIES OF PROTONATED ACETYLENE $C_2H_3^+$...................15 min.(1:47)

    R. ESCRIBANO and P. R. BUNKER, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

RE3. THE PUZZLING INFRARED SPECTRUM OF A CARBONIUM ION ($C_2H_3^+$?).................15 min.(2:04)

    M. W. CROFTON, B. D. REHFUSS, B. M. DINELLI, and T. OKA, Department of Chemistry and Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois, 60637.

RE4. ANALYSIS OF THE ν_2 BAND OF D_3^+..10 min.(2:21)

    S. C. FOSTER, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; A.R.W. McKELLAR, and J.K.G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

RE5. HIGH-J LINES IN THE ν_2 BAND OF H_3^+..15 min.(2:33)

    W. A. MAJEWSKI, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260; M. D. MARSHALL, A.R.W. McKELLAR, and J.K.G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

RE6. A MORSE OSCILLATOR ADAPTED ROTATION-VIBRATION HAMILTONIAN FOR H_3^+............15 min.(2:50)

    PER JENSEN, Department of Chemistry, University of Aarhus, Aarhus, Denmark; V. SPIRKO, Institute of Physical Chemistry, Czechoslovak Academy of Science, Prague, Czechoslovakia; and P. R. BUNKER, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

Intermission

RE7. MEASUREMENT OF THE ν_4 VIBRATION OF AMMONIUM BY VELOCITY MODULATION DIODE LASER SPECTROSCOPY..10 min.(3:25)

    M. POLAK, M. GRUEBELE, and R. J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720.

RE8. INFRARED SPECTRUM OF THE ν_3 BAND OF CH_3^+......................................15 min.(3:37)

    M. W. CROFTON, M.-F. JAGOD, B. D. REHFUSS, T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois, 60637; and W. A. KREINER, Department of Physical Chemistry, University of Ulm, Ulm, Federal Republic of Germany.

RE9. ANALYSIS OF THE ν_3 INFRARED FUNDAMENTAL BAND OF H_2O^+ (X $^2B_1$).................15 min.(3:54)

    B. M. DINELLI, M. W. CROFTON, and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois, 60637. Permanent address of Dinelli: Istituto di Spettroscopia Molecolare del C.N.R., Bologna, Italy.

RE10. MEASUREMENT OF THE 01^10-11^10 BENDING HOT BAND AND OTHER WEAK BANDS OF HCS^+ BY VELOCITY MODULATION LASER SPECTROSCOPY............................10 min.(4:11)

    N. H. ROSENBAUM, J. C. OWRUTSKY, E. KEIM, L. M. TACK, and R. J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720.

RE11. MEASUREMENT OF THE VIBRATION-ROTATION SPECTRUM OF THE AMIDE ANION BY VELOCITY MODULATION LASER SPECTROSCOPY...................................15 min.(4:23)

    L. M. TACK, N. H. ROSENBAUM, J. C. OWRUTSKY, and R. J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720.

RE12. VELOCITY MODULATION LASER SPECTROSCOPY OF VIBRATIONALLY EXCITED CF^+: DETERMINATION OF THE MOLECULAR POTENTIAL FUNCTION...........................10 min.(4:50)

    M. GRUEBELE, M. POLAK, and R. J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720.

THURSDAY, JUNE 19, 1986 — 1:30 P.M.

Room 1005, Physics Laboratory

Chairman: ROBERT J. GLINSKI, National Center for Atmospheric Research, Boulder, Colorado.

RF1. CURVILINEAR COORDINATE FORMULATION FOR THE VIBRATION-ROTATION-
LARGE AMPLITUDE INTERNAL MOTION INTERACTIONS WITH APPLICATION
TO THE WATER MOLECULE.. 5 min.(1:30)

YUHUA GUAN and C. RICHARD QUADE, Department of Physics, Texas Tech
University, Lubbock, Texas, 79409.

RF2. $H_2^{18}O$: THE (041), (220), (121), (022), (300), (201), (102), AND (003)
INTERACTING STATES. LINE INTENSITIES BETWEEN 9 500 AND 11 500 cm^{-1}.........10 min.(1:37)

J.-P. CHEVILLARD, J.-Y. MANDIN, J.-M. FLAUD, and C. CAMY-PEYRET,
Laboratoire de Physique Moléculaire et Optique Atmosphérique, CNRS,
Campus d'Orsay, 91405 Orsay, France.

RF3. THE ν_2 BAND OF HDO: LINE POSITIONS AND INTENSITIES.........................10 min.(1:49)

C. CAMY-PEYRET, J.-M. FLAUD, and A. MAHMOUDI, Laboratoire de
Physique Moléculaire et d'Optique Atmosphérique, Campus d'Orsay,
91405 Orsay, France.

RF4. LINE POSITIONS AND STRENGTHS OF HDO AND D_2O IN THE (010) AND
(020) - (010) BANDS..10 min.(2:01)

R. A. TOTH, Jet Propulsion Laboratory, MS 183-301, 4800 Oak Grove
Drive, Pasadena, California, 91109.

RF5. TEMPERATURE DEPENDENCE OF N_2-BROADENED HALFWIDTHS OF H_2O....................10 min.(2:13)

ROBERT R. GAMACHE, Center for Atmospheric Research, University of
Lowell, Lowell, Massachusetts, 01854; and LAURENCE S. ROTHMAN,
Optics Division, Air Force Geophysics Laboratory, Hanscom Air Force
Base, Massachusetts, 01731.

Intermission

RF6. DIODE LASER MEASUREMENTS IN THE ν_1 BAND OF $^{16}O_3$.............................10 min.(2:40)

M.A.H. SMITH, C. P. RINSLAND, Atmospheric Sciences Division, MS 401A,
NASA/Langley Research Center, Hampton, Virginia, 23665-5225;
K. B. THAKUR, Department of Physics, The Ohio State University,
Columbus, Ohio, 43210; V. MALATHY DEVI, and D. CHRIS BENNER,
Department of Physics, College of William and Mary, Williamsburg,
Virginia, 23185.

RF7. INTENSITIES AND SELF-BROADENING OF OZONE NEAR 5 μm.........................10 min.(2:52)

M.A.H. SMITH, C. P. RINSLAND, Atmospheric Sciences Division, MS 401A,
NASA/Langley Research Center, Hampton, Virginia, 23665-5225;
V. MALATHY DEVI, and D. CHRIS BENNER, Department of Physics, College
of William and Mary, Williamsburg, Virginia, 23185.

RF8. THE ν_1 AND ν_3 BANDS OF $^{18}O^{16}O^{18}O$ AND $^{18}O^{18}O^{18}O$.............................10 min.(3:04)

J. M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et
d'Optique, Atmosphérique, Campus d'Orsay, 91405 Orsay, France;
V. MALATHY DEVI, Department of Physics, College of William and Mary,
Williamsburg, Virginia, 23185; C. P. RINSLAND, and M.A.H. SMITH,
NASA/Langley Research Center, MS 401A, Hampton, Virginia, 23665.

RF9. LINE STRENGTHS AND PRESSURE BROADENING WIDTHS OF SOME SELECTED NO_2
LINES OF ATMOSPHERIC IMPORTANCE USING DIODE LASER SPECTROSCOPY...............15 min.(3:16)

A. FRIED and R. L. SAMS, Center for Analytical Chemistry, Gas and
Particulates Division, National Bureau of Standards, Gaithersburg,
Maryland, 20899.

RF10. RESEARCH ON THE IR ABSORPTION OF WATER DIMER............................. 5 min.(3:33)

SHANXIONG SHEN, CAI PEIPEI, ZHANG HANSHENG, and I-SHAN ZHENG,
Department of Physics, East-China Normal University, Shanghai,
200062, People's Republic of China.

RF11. Π8 will be presented here (J. M. HARTMANN)..................................15 min.(3:40)

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Chairman Before Intermission: W. L. MEERTS, Fysisch Laboratorium, Katholieke Universiteit, Nijmegen, The Netherlands.

Chairman After Intermission: NORMAN C. CRAIG, Department of Chemistry, Oberlin College, Oberlin, Ohio.

RG1.   SPECTROSCOPY OF SMALL, FUNDAMENTAL SPECIES IN THE MILLIMETER WAVE
       REGION USING A BROADBAND SPECTROMETER..15 min.(1:30)

           RANDY A. BOOKER, ERIC HERBST, FRANK C. DE LUCIA, Department of Physics,
           Duke University, Durham, North Carolina, 27706; JOHN G. BAKER,
           Schuster Laboratory, The University, Manchester, United Kingdom,
           M13 9PL; and K.V.L.N. SASTRY, Department of Physics, University
           of New Brunswick, Fredericton, New Brunswick, Canada, E3B 5A3.

RG2.   TIME RESOLVED ROTATIONAL ENERGY TRANSFER IN $^{13}CH_3F$..........................15 min.(1:47)

           RODNEY I. McCORMICK, FRANK C. DE LUCIA, Department of Physics, Duke
           University, Durham, North Carolina, 27706; and DAVID D. SKATRUD,
           United States Army Research Office, Research Triangle Park, North
           Carolina, 27709.

RG3.   HYPERFINE CALCULATIONS USING AN UNCOUPLED REPRESENTATION.....................15 min.(2:04)

           S. YOUNG, Department of Chemistry, University of South Alabama,
           Mobile, Alabama, 36688; and S. KUKOLICH, Department of Chemistry,
           University of Arizona, Tucson, Arizona, 85721.

RG4.   MICROWAVE SPECTRA AND MOLECULAR STRUCTURE OF 1,1,2,2-TETRAFLUOROCYCLO-
       PROPANE..15 min.(2:21)

           R. N. BEAUCHAMP, C. W. GILLIES, Department of Chemistry, Rensselaer
           Polytechnic Institute, Troy, New York, 12180; and N. C. CRAIG,
           Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074.

RG5.   MICROWAVE SPECTRUM OF CIS-1,1,2,3-TETRAFLUOROCYCLOPROPANE...................10 min.(2:38)

           R. N. BEAUCHAMP, J. ZOZOM, and C. W. GILLIES, Department of Chemistry,
           Rensselaer Polytechnic Institute, Troy, New York, 12180.

RG6.   MICROWAVE SPECTRUM OF 3-FLUORO-2-METHYLPROPENE.............................15 min.(2:50)

           T. S. LITTLE, H. QIU, J. R. DURIG, Department of Chemistry, University
           of South Carolina, Columbia, South Carolina, 29208; and MENGZHANG ZHEN,
           The Institute of the Liming Chemical Industry, Luoyang, Henan Province,
           People's Republic of China.

Intermission

RG7.   MICROWAVE SPECTRA OF EIGHT ISOTOPIC SPECIES OF ETHYLPHOSPHINE...............15 min.(3:25)

           P. GRONER, R. D. JOHNSON, and J. R. DURIG, Department of Chemistry,
           University of South Carolina, Columbia, South Carolina, 29208.

RG8.   MICROWAVE SPECTRUM, STRUCTURE AND DIPOLE MOMENT OF TRIFLUOROMETHYL SILANE...15 min.(3:42)

           G. ATTIA, P. GRONER, J. R. DURIG, Department of Chemistry, University
           of South Carolina, Columbia, South Carolina, 29208; and H. BURGER,
           Anorganische Chemie, Universität–Gesamthochschule, 5600 Wuppertal,
           West Germany.

RG9.   MILLIMETER-WAVE OPTICAL DOUBLE RESONANCE SPECTRA OF NO_2:
       IS N A GOOD QUANTUM NUMBER?...10 min.(3:59)

           STEPHEN L. COY, Department of Chemistry, Harvard University, Cambridge,
           Massachusetts, 02138; KEVIN K. LEHMANN, Department of Chemistry,
           Princeton University, Princeton, New Jersey, 08544; and FRANK C. DE LUCIA,
           Department of Physics, Duke University, Durham, North Carolina, 27706.

RG10. MICROWAVE ANTICROSSING SPECTRUM OF AMMONIA..................................15 min.(4:11)

           I. OZIER, Department of Physics, The University of British Columbia,
           Vancouver, British Columbia, Canada, V6T 2A6; and W. L. MEERTS,
           Fysisch Laboratorium, Katholieke Universiteit, Toernooiveld,
           6525 ED Nijmegen, The Netherlands.

RG11. ACCIDENTAL 3-LEVEL DOUBLE RESONANCES IN THE 6-μm LASER-STARK
       SPECTRUM OF $^{15}NH_3$...10 min.(4:28)

           W. H. WEBER, Department of Physics, Research Staff, Ford Motor
           Company, Dearborn, Michigan, 48121.

RG12. AMMONIA VIBRATIONAL BANDS BETWEEN 6500 cm^{-1} AND 12000 cm^{-1}:
ROTATIONAL ASSIGNMENT BASED ON MICROWAVE-OPTICAL DOUBLE RESONANCE............10 min.(4:40)

STEPHEN L. COY, Department of Chemistry, Harvard University, Cambridge,
Massachusetts, 02138; and KEVIN K. LEHMANN, Department of Chemistry,
Princeton University, Princeton, New Jersey, 08544.

RG13. TRANSITION DIPOLE MOMENT MEASUREMENTS FOR THE ν_2 BAND OF NH_3
WITH MOLECULAR BEAM LASER STARK SPECTROSCOPY.......Arrived Late............10 min.(4:52)

W. Q. CAI, T. E. GOUGH, X. J. GU, N. R. ISENOR, and G. SCOLES,
Center for Molecular Beam and Laser Chemistry, University of
Waterloo, Waterloo, Ontario, Canada, N2L 3G1.

RG14. Π10 will be presented here (M. OLDANI).....................................15 min.(5:04)

THURSDAY, JUNE 19, 1986 -- 1:30 P.M.

Room 1008, Evans Chemical Laboratory

Chairman Before Intermission: DONALD A. CHERNOFF, Corporate Research Center, The Standard Oil Company (Ohio), Warrensville Heights, Ohio.

Chairman After Intermission: R. J. LE ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

RH1. DIRECT DETERMINATION OF LONG-RANGE INVERSE-POWER POTENTIAL COEFFICIENTS FROM VIBRATIONAL ENERGIES AND B_v VALUES.......................................15 min.(1:30)

   J. SHELLEY and R. J. LE ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.

RH2. DETERMINING AN ATTRACTIVE DIATOM POTENTIAL WELL BY INVERSION OF BOUND-CONTINUUM EMISSION INTENSITIES.....................................15 min.(1:47)

   R. J. LE ROY and WILLIAM J. KEOGH, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.

RH3. VIBRATIONAL FREQUENCY SHIFTS OF SF_6 MOLECULES INSIDE AND ON THE SURFACE OF SOLID MATRICES OR MOLECULAR CLUSTERS.....................................15 min.(2:04)

   D. EICHENAUER and R. J. LE ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.

RH4. ANALYSIS OF METROPOLIS MONTE CARLO STUDIES OF A MODEL ICE Ih................15 min.(2:21)

   P. W. DEUTSCH, The Pennsylvania State University at Beaver, Brodhead Road, Monaca, Pennsylvania, 15061.

RH5. AB INITIO CALCULATION OF THE IR INTENSITIES OF STRETCHING VIBRATIONS OF COS AND CS_2..10 min.(2:38)

   P. BOTSCHWINA and P. SEBALD, Fachbereich Chemie der Universität Kaiserslautern, D-6750 Kaiserslautern, West Germany.

Intermission

RH6. ELECTRONIC SPECTRA OF ArH AND XeH..15 min.(3:10)

   R. H. LIPSON, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

RH7. RADIATIVE LIFETIME MEASUREMENTS FOR THE B $^3\pi(0^+)$ STATE OF CHLORINE MONOFLUORIDE...15 min.(3:27)

   L. J. VAN DE BURGT and M. C. HEAVEN, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, 60616.

RH8. LOW PRESSURE PHOTOACOUSTIC SPECTROSCOPY OF SMALL MOLECULES IN WHICH THE RF DISCHARGE IS USED AS SONIC SENSOR.....................................15 min.(3:44)

   D. KUMAR, P. L. CLANCY, L. KLASINC, R. V. NAUMAN, and S. P. McGLYNN, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, 70803.

RH9. ELECTRONIC SPECTROSCOPY OF THE CYANOGEN HALIDES.............................15 min.(4:01)

   S. FELPS and S. P. McGLYNN, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, 70803.

RH10. PULSED LASER OPTOGALVANIC SPECTROSCOPY OF IODINE IN RF DISCHARGE............15 min.(4:18)

   D. KUMAR, L. KLASINC, P. L. CLANCY, R. V. NAUMAN, and S. P. McGLYNN, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, 70803.

RH11. PULSED LASER OPTOGALVANIC SPECTROSOCPY OF BROMINE IN RF DISCHARGE..........15 min.(4:35)

   D. KUMAR, L. KLASINC, P. L. CLANCY, R. V. NAUMAN, and S. P. McGLYNN, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, 70803.

RH12. π4 will be presented here (J. W. HEPBURN)...................................10 min.(4:52)

FRIDAY, JUNE 20, 1986 — 8:30 A.M.

Room 1153, Physics Laboratory

Chairman: C. P. RINSLAND, NASA/Langley Research Center, Hampton, Virginia.

FA1.   ROTATIONAL SPECTRA OF MOLECULAR IONS USING TUNABLE DIODE LASER..............15 min.(8:30)

DI-JIA LIU, WING-CHEUNG HO, and TAKESHI OKA, Department of Chemistry
and Department of Astronomy and Astrophysics, The University of
Chicago, Chicago, Illinois, 60637.

FA2.   ROTATIONAL SPECTROSCOPY OF MOLECULAR IONS WITH TUNABLE FAR INFRARED
LASERS...10 min.(8:47)

K. B. LAUGHLIN, G. A. BLAKE, R. COHEN, and R. J. SAYKALLY, Department
of Chemistry, University of California, Berkeley, California, 94720.

FA3.   MEASUREMENT OF THE VIBRATION-ROTATION SPECTRUM OF THE HYDROXIDE ANION
(OH$^-$) BY VELOCITY MODULATION LASER SPECTROSCOPY.............................10 min.(8:59)

N. H. ROSENBAUM, J. C. OWRUTSKY, L. M. TACK, and R. J. SAYKALLY,
Department of Chemistry, University of California, Berkeley,
California, 94720.

FA4.   INFRARED SPECTRUM OF THE FUNDAMENTAL VIBRATION-ROTATION BAND OF OD$^-$.........15 min.(9:11)

B. D. REHFUSS, M. W. CROFTON, and T. OKA, Department of Chemistry and
Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois,
60637.

FA5.   DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF MOLECULAR IONS...................20 min.(9:28)

T. NAKANAGA and T. AMANO, Herzberg Institute of Astrophysics, National
Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

FA6.   PLASMA DIAGNOSIS USING INFRARED SPECTROSCOPY: ANOMALOUSLY HIGH POPULATION
OF THE v=3 LEVEL AND DOUBLING OF ArH$^+$ SPECTRAL LINES DUE TO DOPPLER
SHIFT IN AN AC DISCHARGE..15 min.(9:45)

DI-JIA LIU, WING-CHEUNG HO, and TAKESHI OKA, Department of Chemistry
and Astronomy and Astrophysics, The University of Chicago, Chicago,
Illinois, 60637.

Intermission

FA7.   AN ATTEMPT TO MEASURE ELECTRIC FIELD IN A D.C. GLOW DISCHARGE USING
SUB-DOPPLER INFRARED SPECTRUM OF CH_3F..................................15 min.(10:20)

FU-SHIH PAN, W. A. KREINER, and T. OKA, Department of Chemistry and
Astronomy and Astrophysics, The University of Chicago, Chicago,
Illinois, 60637.

FA8.   PRECISE MEASUREMENT OF FINE STRUCTURE INTERVALS IN ATOMIC IONS BY LASER
MAGNETIC RESONANCE SPECTROSCOPY: N$^+$ AND C$^+$.................................10 min.(10:37)

A. L. COOKSY, D. C. HOVDE, G. A. BLAKE, and R. J. SAYKALLY, Department
of Chemistry, University of California, Berkeley, California, 94720.

FA9.   INFRARED SPECTRUM OF THE RENNER-TELLER ACTIVE v_2 BAND OF $X^2\Pi_g CO_2^+$..........15 min.(10:49)

T. J. SEARS, Department of Chemistry, Brookhaven National Laboratory,
Upton, New York, 11973.

FA10. OBSERVATION OF THE $v_2 = 2^+ \leftarrow 1^-$ HOT BAND OF H_3O^+..........................15 min.(11:06)

T. J. SEARS, Department of Chemistry, Brookhaven National Laboratory,
Upton, New York, 11973; P. B. DAVIES, and S. A. JOHNSON, Physical
Chemistry Department, University of Cambridge, Cambridge, CB2 1EP,
England.

FA11. AN AB INITIO CALCULATION OF THE EQUILIBRIUM GEOMETRY AND BARRIER HEIGHT
TO INVERSION OF H_3O^+ AND THE PROTON AFFINITY OF H_2O........................ 5 min.(11:23)

P. BOTSCHWINA, Fachbereich Chemie der Universität Kaiserslautern,
D-6750 Kaiserslautern, West Germany.

FA12. MEASUREMENT OF THE v_4 BAND OF H_3O^+ BY VELOCITY MODULATION DIODE LASER
SPECTROSCOPY...10 min.(11:30)

M. GRUEBELE, M. POLAK, and R. J. SAYKALLY, Department of Chemistry,
University of California, Berkeley, California, 94720.

FA13. AB INITIO CALCULATION OF POTENTIAL ENERGY SURFACES AND SPECTROSCOPIC
PROPERTIES OF H_2S AND H_3S^+..15 min.(11:42)

P. BOTSCHWINA, Fachbereich Chemie der Universität Kaiserslautern,
D-6750 Kaiserslautern, West Germany; A. ZILCH, H.-J. WERNER,
P. ROSMUS, and E.-A. REINSCH, FB Chemie der Univ. Frankfurt,
D-6000 Frankfurt, West Germany.

FA14. Ill will be presented here (K. B. LAUGHLIN)................................10 min.(11:59)

FRIDAY, JUNE 20, 1986 — 8:30 A.M.

Room 1009, Physics Laboratory

Chairman: BRADLEY M. STONE, Department of Chemistry, San Jose State University, San Jose, California.

FB1. TIME-RESOLVED STUDIES OF INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION IN S_1 BENZENE...15 min.(8:30)

DAVID B. MOSS and CHARLES S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

FB2. IVR IN S_1 p-FLUOROTOLUENE...15 min.(8:47)

R. J. LONGFELLOW, D. B. MOSS, C. S. PARMENTER, and B. M. STONE, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

FB3. INFRARED SPECTROSCOPY OF SMALL MOLECULES ADSORBED ON SODIUM CHLORIDE SURFACES...15 min.(9:04)

H. H. RICHARDSON, J. A. EDLING, and G. E. EWING, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

FB4. TRANSFER AND STORAGE OF VIBRATIONAL ENERGY IN LIQUIDS: COLLISIONAL UP-PUMPING OF CARBON MONOXIDE IN LIQUID ARGON..............................15 min.(9:21)

DEON S. ANEX and GEORGE E. EWING, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

FB5. COLLISIONAL RELEASE OF Br_2..10 min.(9:38)

J. E. SMEDLEY, S. R. LEONE, Joint Institute for Laboratory Astrophysics and Department of Chemistry, Boulder, Colorado, 80309-0440; and H. K. HAUGEN, Department of Physics, University of Toronto, Toronto, Ontario, Canada, M5S 1A7.

FB6. EVOLUTION OF N_2 EXCITED STATE VIBRATIONAL LEVEL POPULATIONS IN A PULSED ELECTRIC DISCHARGE..15 min.(9:50)

J. S. MORRILL and W. M. BENESCH, Institute for Molecular Physics, University of Maryland, College Park, Maryland, 20742.

Intermission

FB7. HIGH-TEMPERATURE QUENCHING OF CH ($A^2\Delta,v'=0$)................................15 min.(10:20)

NANCY L. GARLAND and DAVID R. CROSLEY, Molecular Physics Department, SRI International, Menlo Park, California, 94025.

FB8. SLOW INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION (IVR) IN ISOLATED BENZENE MOLECULES...15 min.(10:37)

DONALD A. CHERNOFF, J. GARY PRUETT, Corporate Research Center, The Standard Oil Company (Ohio), 4440 Warrensville Center Road, Warrensville Heights, Ohio, 44128; and JAMES D. MYERS, Department of Chemistry, University of California, Berkeley, California, 94720.

FB9. $\Sigma2$ will be presented here (J. V. COE)..15 min.(10:54)

FB10. $\Sigma3$ will be presented here (J. T. SNODGRASS)....................................15 min.(11:11)

FRIDAY, JUNE 20, 1986 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chairman Before Intermission: R. SOORYAKUMAR, Department of Physics, The Ohio State University, Columbus, Ohio.

Chairman After Intermission: WON B. ROH, Department of Engineering Physics, Air Force Institute of Technology, Wright-Patterson AFB, Ohio.

FC1. CALCULATION OF THE COMPLETE SET OF OBSERVABLES FOR ELASTIC LIGHT SCATTERING BY RANDOMLY ORIENTED MACROMOLECULES..............................15 min.(8:30)

W. M. McCLAIN and W. A. GHOUL, Department of Chemistry, Wayne State University, Detroit, Michigan, 48202.

FC2. A NEW METHOD FOR THE ANALYSIS OF CARS LINESHAPES...........................15 min.(8:47)

J. M. BOSTICK and L. A. CARREIRA, Department of Chemistry, University of Georgia, Athens, Georgia, 30602.

FC3. HIGH-RESOLUTION CARS MEASUREMENT OF RAMAN LINEWIDTHS OF DEUTERIUM...........10 min.(9:04)

DAVID A. RUSSELL and WON B. ROH, Department of Engineering Physics, Air Force Institute of Technology, Wright-Patterson AFB, Ohio, 45433.

FC4. VIBRATIONAL ASSIGNMENTS FOR THE LOW FREQUENCY RAMAN ACTIVE PHONONS IN TCNQ SINGLE CRYSTALS...15 min.(9:16)

K. M. WHITE, K.-H. BROSE, and C. J. ECKHARDT, Department of Chemistry, University of Nebraska, Lincoln, Nebraska, 68588-0304.

FC5. LOW TEMPERATURE MODULATED PIEZOREFLECTION SPECTRA OF TWO POLYDIACETYLENE SINGLE CRYSTALS: PTS AND DCHD...15 min.(9:33)

M. MORROW and C. J. ECKHARDT, Department of Chemistry, University of Nebraska, Lincoln, Nebraska, 68588-0304.

Intermission

FC6. SURFACE-ENHANCED RAMAN SPECTROSCOPY OF BILIRUBIN...........................15 min.(10:10)

YOU-ZUNG HSIEH and MICHAEL D. MORRIS, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

FC7. SURFACE-ENHANCED RAMAN SPECTROSCOPY OF FLAVINS AND FLAVOPROTEINS.............15 min.(10:27)

NAM-SOO LEE and MICHAEL D. MORRIS, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

FC8. SURFACE ENHANCED RAMAN SPECTRA FROM FLAVINS ADSORBED ON A SILVER ELECTRODE: OBSERVATION OF UNSTABLE SEMIQUINONE INTERMEDIATE...........................10 min.(10:44)

J. XU, R. L. BIRKE, and J. R. LOMDARDI, Department of Chemistry, City College of New York, New York, New York, 10031.

FC9. VIBRATIONAL SPECTRA AND CONFORMATIONS OF CYCLOHEXYLPHOSPHINE AND 2-CYANOETHYLPHOSPHINE..15 min.(10:56)

V. F. KALASINSKY and T.-H. PAI, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi, 39762.

Π12 will be presented as FC2 which has been cancelled (G.N.R. TRIPATHI).....15 min.

FC10. Π13 will be presented here (J. SOBHANADRI).................................10 min.(11:13)

Σ SESSION

PLEASE NOTE: The following papers arrived late, well after the program has been organized
and typing progressed significantly. The sessions in which they are scheduled for presentation
are indicated in parentheses in the righthand margin.

Σ1.   PHOTOELECTRON SPECTROSCOPY OF N_2O^-, CO_2^-, $(N_2O)_2^-$ AND $(CO_2)_2^-$...................15 min.(TC11)

K. H. BOWEN, J. V. COE, J. T. SNODGRASS, C. B. FREIDHOFF, and
K. M. McHUGH, Department of Chemistry, The Johns Hopkins University,
Baltimore, Maryland, 21218.

Σ2.   PHOTOELECTRON SPECTROSCOPY OF $(H_2O)_n^-$.......................................15 min.(FB9)

J. V. COE, K. H. BOWEN, Department of Chemistry, The Johns Hopkins
University, Baltimore, Maryland, 21218; and D. R. WORSNOP,
Aerodyne Corporation, Billerica, Massachusetts, 01821-3976.

Σ3.   NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF P_2^-...............................15 min.(FB10)

J. T. SNODGRASS, J. V. COE, C. B. FREIDHOFF, K. M. McHUGH, and
K. H. BOWEN, Department of Chemistry, The Johns Hopkins University,
Baltimore, Maryland, 21218.

Σ4.   SYMMETRY CLASSIFICATION OF THE ROTATION-VIBRATION ENERGY LEVELS IN
AMMONIA DIMER...10 min.(TF14)

D. D. NELSON, JR. and W. KLEMPERER, Department of Chemistry,
Harvard University, Cambridge, Massachusetts; and G. T.
FRASER, Molecular Spectroscopy Division, National Bureau of
Standards, Washington, D.C., 20234.

Σ5.   INVERSION EFFECTS IN THE QUADRUPOLE HYPERFINE SPECTRUM OF
D_2O-CO...10 min.(TF15)

K. I. PETERSON, D. J. YARON, and W. KLEMPERER, Department
of Chemistry, Harvard University, Cambridge, Massachusetts,
02138.

II SESSION

PLEASE NOTE: The following papers arrived after the program was sent to the printers.
The sessions in which they are scheduled for presentation are indicated in the right-
hand margin.

II1.   VIBRATIONAL CIRCULAR DICHROISM OF SUBSTITUTED ALLENES.....................10 min.(RC13)

T. A. KEIDERLING, U. NARAYANAN, J. S. CHICKOS,
W. RUNGE, and C. J. ELSEVIER, Department of Chemistry,
University of Illinois at Chicago, Box 4348, Chicago,
Illinois, 60680.

II2.   INTRACONFIGURATIONAL ABSORPTION SPECTROSCOPY OF IrX_6^{2-} IN A_2MX_6
TYPE HOST CRYSTALS...10 min. (TC12)

R. K. YOO and T. A KEIDERLING, Department of Chemistry,
University of Illinois at Chicago, Box 4348, Chicago,
Illinois, 60680.

II3.   EXTENSION OF VCD MEASUREMENTS TOWARDS THE FAR IR..........................10 min.(RC12)

GÜNTER GEORG HOFFMANN, Lehrstuhl für Physikalische und
Theoretische Chemie, Universität Essen, Gesamthochschule,
D-4300 Essen 1, West Germany.

II4.   VACUUM ULTRAVIOLET LASER SPECTROSCOPY OF PERTURBED $^2\Delta$ STATES IN NO........10 min.(RH12)

J. W. HEPBURN and D. HART, Centre for Molecular Beam and
Laser Chemistry, University of Waterloo, Waterloo,
Ontario, Canada, N2L 3G1.

II5.   PRODUCTION OF CLUSTERS BY PULSED LASER VAPORIZATION AND THEIR
TRAPPING IN RARE GAS MATRICES...10 min.(MG'9)

M. RASENAN, L. A. HEINBROOK, and V. E. BONDYBEY,
AT&T Bell Laboratories, Murray Hill, New Jersey,
07974.

II6.   THE INFRARED SPECTRUM AND NORMAL COORDINATE ANALYSIS OF THE
BICARBONATE ION..10 min.(ME13)

HOWARD COKER, Department of Chemistry, University of
South Dakota, Vermillion, South Dakota, 57069; and
WILLIAM KEARNEY, Department of Chemistry, University
of Iowa, Iowa City, Iowa, 52240.

II7.   EMISSION SPECTROSCOPY OF IF $A^3\Pi(1)$: MEDIUM RESOLUTION VIBRA-
TIONAL ANALYSIS..15 min.(MF14)

B. D. McFEETERS, Advanced Chemical Laser Branch, Air
Force Weapons Laboratory, Kirtland AFB, New Mexico,
87117-6008; and P. J. WOLF, Defense Nuclear Agency,
Shock Physics and Aerospace Systems, Washington, D.C.,
20305-1000.

II8.   NEW CALCULATIONS AND HIGH-TEMPERATURE MEASUREMENTS OF H_2O
COLLISIONAL-BROADENING...15 min.(RF11)

J. M. HARTMANN, J. TAINE, Laboratoire d'Energétique
Moléculaire et Macroscopique, Combustion, Ecole Centrale
des Arts et Manufactures, Grande voie des vignes,
92295 Chatenay-Malabry, France; and J. BONAMY,
B. LABANI, and D. ROBERT, Laboratoire de Physique
Moléculaire, Faculté des Sciences et Techniques,
25030 Besançon Cedex, France.

II9.   THE ν_2 BAND OF HOBr...10 min.(ME14)

E. A. COHEN and G. A. McRAE, Jet Propulsion Laboratory,
California Institute of Technology, 4800 Oak Grove
Drive, Pasadena, California 91109.

Π10. MICROWAVE FOURIER TRANSFORM SPECTROSCOPY.................................15 min.(RG14)

   M. OLDANI, B. VOGELSANGER, and A. BAUDER,
   Laboratorium für Physikalische Chemie, Eidgenössische
   Technische Hochschule Zürich, Universitätstrasse 22,
   CH-8092 Zürich, Switzerland.

Π11. MEASUREMENT OF ROTATIONAL SPECTRA, ROTATIONAL G-FACTORS, AND
THE EQUILIBRIUM BOND LENGTH FOR ArH$^+$ BY TUNABLE FAR-INFRARED
LASER SPECTROSCOPY...10 min.(FA14)

   K. B. LAUGHLIN, G. A. BLAKE, R. COHEN, and
   R. J. SAYKALLY, Department of Chemistry, University
   of California, Berkeley, California, 94720.

Π12. RESONANCE RAMAN SPECTROSCOPY OF TRANSIENT RADICAL CATIONS.................15 min.(FC2)

   G.N.R. TRIPATHI, Radiation Laboratory, University of
   Notre Dame, Notre Dame, Indiana, 46556.

Π13. INFRARED AND RAMAN BAND SHAPES AND MOLECULAR DYNAMICS IN
LIQUID PICOLINES...10 min.(FC10)

   J. SOBHANADRI, Department of Physics, Indian Institute
   of Technology, Madras, India, and Radiation Laboratory,
   University of Notre Dame, Notre Dame, Indiana, 46556.

ME1.   (1:30)

A MULTIPLE REFLECTION CELL TO ENHANCE DIRECT IR ABSORPTION IN A COLLIMATED MOLECULAR BEAM

D. KAUR, A. M. DE SOUZA AND D. S. PERRY

Direct absorption measurements using an F-center laser are carried out in a collimated molecular beam. Absorbance is increased by passing the laser beam up to 80 times through the molecular beam.

The multiple reflection cell consists of two spherical concave mirrors in a near-concentric alignment. The laser beam, directed slightly off-axis into the cell, forms a parabolic spot pattern on each mirror. The laser beam reflections collectively form a waist at the center of the cell. The dimension of the waist and the number of reflections can be adjusted independently, enabling efficient coupling to a collimated molecular beam.

High resolution sub-Doppler spectra of methyl acetylene with a line width of 35 MHz have been obtained in the 3 micron region.

Address: Department of Chemistry, University of Rochester, Rochester, NY 14627

ME2.   (1:42)

HIGH RESOLUTION INFRARED SPECTROSCOPY OF LiCl AT 800°C

G.A.THOMPSON, A.G.MAKI, Wm.B.OLSON, A.WEBER

We have measured infrared absorption spectra of gas phase LiCl, in natural isotopic abundance, at about 800°C. Over 600 $\Delta v=1$ transitions were measured at a resolution of 0.006 cm^{-1} in the 500 to 700 cm^{-1} spectral region using a Bomem Fourier transform spectrometer with appropriate transfer optics for including a 1.5 meter heat pipe in the instrument's optical path. Some $\Delta v=2$ transitions were also observed with Doppler limited resolution using a tunable diode laser. These data, along with microwave data taken from the literature, were fit to a Dunham potential and used to calculate a set of Dunham Y's. Attempts to measure other diatomics will be made.

Address of Thompson, Maki, Olson, and Weber: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Md, 20899.

ME3.   (1:59)

HIGH RESOLUTION SPECTRUM OF THE ν_2 AND $2\nu_6$ BANDS OF $^{28}SiH_3D$

R. D. SCHAEFFER, R. W. Lovejoy, W. B. Olson, G. Tarrago

The ν_2 and $2\nu_6$ bands of $^{28}SiH_3D$ have been recorded between 1450 and 1710 cm^{-1} with 0.005 cm^{-1} apodized resolution using the NBS DA 3.002 BOMEM Fourier transform spectrometer. Assignments made to the ν_2 band range from $J=0{\rightarrow}25$ and $K=0{\rightarrow}15$. Assignments made to the $2\nu_6^*$ component range from $J=0{\rightarrow}20$ and $K=0{\rightarrow}10$ while the very weak $2\nu_6^2$ band has been assigned predominantly through interaction with the other components. Very strong perturbations were observed in the $K=0$ and $K=1$ levels of $2\nu_6^*$ which arose through interactions with the $k\ell=+4$ and the $k\ell=+6$ states respectively of $2\nu_6^2$. The $K=2$ and $K=10$ levels of ν_2 were also found to be strongly interacting with $k\ell=-6$ and $k\ell=-16$ levels respectively of $2\nu_6^2$. Observed transitions were fit using ground state constants, obtained through fitting of combination differences, and upper state energy levels calculated by diagonalizing an energy matrix including Fermi resonance terms between $V_2=1$ and $V_6=2$. The band center for the ν_2 band was found to be 1593.967 cm^{-1} while the $2\nu_6^*$ band center lies at 1557.257 cm^{-1}. Other molecular constants will be reported.

Address of Schaeffer and Lovejoy: Lehigh University, Chemistry Department, Bethlehem, PA 18015.
Address of Olson: National Bureau of Standards, Gaithersburg, MD 20899.
Address of Tarrago: Laboratoire D'Infrarouge, Universite de Paris-Sud, Campus d'Orsay – Bât 350, 91405 Orsay CEDEX, FRANCE.

ME4.   (2:16)

ANALYSIS OF THE ν_{14} BAND OF BENZENE-d_6

J. PLÍVA, A. VALENTIN, J. CHAZELAS, AND L. HENRY

The perpendicular band of the E_{1u} vibration ν_{14} of benzene-d_6 was recorded in the 800 - 830 cm^{-1} region with the aid of a large Fourier transform spectrometer at the Université Pierre et Marie Curie with resolution near the Doppler limit.

$^{P}P_K$ branches up to K = 50 and $^{r}R_K$ branches to K = 39 have been assigned in the ν_{14} band. The $^{r}R_K$ branches for K from 16 to 30 are strongly affected by an x,y-Coriolis resonance, with an avoided crossing observed between K' = 23 and 24. The origin of the state responsible for this perturbation lies above 820 cm^{-1}, close to the reported position of the infrared- and Raman-inactive B_{2u} fundamental ν_{10}. However, a direct first-order interaction between B_{2u} and E_{1u} states is not allowed by symmetry, and alternative interpretations of the observed perturbation, including possible reassignment of the inactive ν_{10} and ν_{19} vibrations, will be discussed. Spectroscopic constants obtained from the analysis will be reported.

Address of Plíva : Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802.
Address of Valentin, Chazelas, and Henry : Laboratoire de Spectronomie Moléculaire CNRS 060136, Université Pierre et Marie Curie, 4 Place Jussieu, 75230 Paris Cedex 05, France.

ME5.   (2:33)

REFILLING TRANSITIONS IN TEA-PUMPED METHANOL FIR LASERS

I. MUKHOPADHYAY, R.M. LEES, AND J.W.C. JOHNS

When high-power TEA CO_2 lasers are used for optical pumping of methanol far-infrared (FIR) lasers, a rich emission spectrum is obtained, with many high-frequency lines. However, there has been little success to date in fitting the observed frequencies into energy level schemes associated with known pump transitions. We propose that a significant number of the observed FIR laser lines can be accounted for as refilling transitions within the V=0 vibrational ground state, involving refilling from a $v_t=1$ excited torsional level into the pumped ground state level. The assignments are in most cases supported to within the reported accuracy of the observed FIR laser frequency by identification of the corresponding transition in high-resolution BOMEM Fourier transform FIR spectra.

Address of Mukhopadhyay and Lees: Department of Physics, University of New Brunswick, Fredericton, N.B., Canada E3B 5A3.
Address of Johns: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

ME6.

THE THREE LOWEST-LYING FUNDAMENTALS OF AMINOBORANE, NH_2BH_2

W.D. ANDERSON, M.C.L. GERRY, L. LEWIS-BEVAN, A.J. MERER and D.M. STEUNENBERG

Aminoborane, NH_2BH_2, is a semi-stable inorganic analogue of ethylene, and has a similar molecular structure. In this work the three lowest-lying fundamentals of gaseous NH_2BH_2 have been recorded at high resolution using a Bomem DA 3.002 FT spectrophotometer. These fundamentals are ν_8, which gives a strong C-type band at 612 cm^{-1} (NH_2 out of plane wag), ν_{12}, a very weak B-type band near 742 cm^{-1} which has a peculiar intensity distribution in its K-structure, and ν_6, the infra-red "inactive" torsional vibration near 820 cm^{-1}, for which one perturbation-induced sub-band has been seen. Basically the ν_{12} and ν_6 fundamentals have no intensity of their own, but obtain their oscillator strengths by various complex interaction mechanisms from the ν_8 fundamental. There are many rotational perturbations between these three vibrational states. The results have been confirmed by an analysis of the A-type overtone $2\nu_8$ at 1223 cm^{-1}.

Address of all authors: Dept of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver B.C., Canada V6T 1Y6.

ME7.

DIODE LASER SPECTRA AND ANALYSIS OF THE $\nu_1-\nu_3$ BAND OF $CF_3{}^{35}C\ell$

S. Giorgianni, R. Visinoni, A. Gambi, S. Ghersetti, A. Bizzarri*, J. Hermanussen* and G. Baldacchini

The difference band $\nu_1-\nu_3$ of $CF_3{}^{35}Cl$ located near 631 cm^{-1} has been investigated few years ago by means of Fourier transform infrared spectroscopy /1/. Because of the limited resolution achieved it has not been possible to resolve the K structure of the P(J) and R(J) multiplets. Subsequently the ν_1 band has been investigated with a diode laser spectrometer, which allowed a precise evaluation of the molecular parameters /2/.

As a part of a continuing effort to investigate the molecular structure of the trifluorochloromethane we measured at a diode laser resolution the $\nu_1-\nu_3$ band in the 622 to 641 cm^{-1} region. The K structure of many P(J) and R(J) manifolds has been resolved and positively identified. The rotational analysis has been extended in the P and R branches up to J = 39 and 47 respectively and more than 650 lines have been assigned. A least-squares fit of the observed transitions to the energy expression including the quartic centrifugal distortion terms was performed and molecular constants for the $\nu_1-\nu_3$ difference band were determined.

From the obtained parameters the vibrational rotational constants of the ν_3 fundamental were derived. Spectra, details of the interpretation and results from the analysis will be presented.

1) H. Bürger, K. Burczyk, R. Grassow and A. Ruoff: J.Mol.Spectrosc. 93, 55 (1982)
2) S. Giorgianni, R. Visinoni, A. Gambi, S. Ghersetti, G. Restelli and F. Cappellani: J.Mol.Spectrosc. 101, 245 (1983)
(*) ENEA guest.

Address of S. Giorgianni et al.: Dipartimento di Spettroscopia, Elettrochimica e Chimica Fisica, Università di Venezia, D.D. 2137, I-30123 Venezia (Italy)
Address of A. Bizzarri et al.: ENEA, TIB, Divisione Fisica Applicata, P.O. Box 64, 00044 Frascati (Rome), Italy.

ME8.   (3:30)

STARK AND ZEEMAN EFFECT OF ETHYLENE OBSERVED BY SUB-DOPPLER SPEC-TROSCOPY

Yit-Tsong CHEN and Takeshi OKA

Recent development of sub-Doppler spectroscopy using microwave modulation sidebands of CO_2 laser radiation has enabled us to perform ultrahigh resolution tunable infrared spectroscopy[1]. Using this technique we studied the small Stark and Zeeman effect of ethylene. Clear Stark splittings have been observed for several low J vibration-rotation lines of the ν_7 band using an electric field of up to 50 KV/cm. The analysis of the Stark pattern has given the following polarizability anisotropy for the ground state:

$$\alpha_{zz} - \frac{\alpha_{xx} + \alpha_{yy}}{2} = 1.42(12)\text{\AA}^3$$

$$\alpha_{xx} - \alpha_{yy} = 0.27(66)\text{\AA}^3$$

The polarizability tensor components for the ν_7 state are considerably different from the ground state, probably because of the near degeneracy of the ν_7 state with other vibrational states (ν_4, ν_8, ν_{10}). More extensive analysis, as well as a study of Zeeman effect to determine the rotational g-factors, are in progress.

[1]Y. T. Chen, J. M. Frye and T. Oka, *J. Opt. Soc. Am. B*, (1986) in press

Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637

ME9.   (3:47)

MAGNETIC FIELD MODULATED INFRARED LASER SPECTROSCOPY OF THE ClH_2^+ ν_2 BAND

K. KAWAGUCHI AND E. HIROTA

The chloronium ion (ClH_2^+) has been detected for the first time in the gas phase by infrared diode laser spectroscopy with magnetic field modulation.

The absorption cell used was 1 m long, 6.5 cm i.d., and of white type multiple reflection type. A hollow cathode of 50 cm length was installed inside a solenoid magnet. A 3.8 kHz AC field of 76G peak-to-peak superimposed on a 37G DC field was employed to modulate the generation of ionic species. The ClH_2^+ ion was produced by a discharge of an H_2 (1 Torr), He (300 mTorr) and HCl (30 mTorr) mixture.

One hundred and forty-eight lines were observed between 1040 cm^{-1} and 1330 cm^{-1}, and 120 lines were assigned to the ν_2 fundamental band of $^{35}ClH_2^+$ and 28 lines to that of $^{37}ClH_2^+$. The observed transitions have been analyzed by Watson's A-reduced Hamiltonian to determine band origins ($\nu_2(^{35}Cl) = 1184.126$ cm^{-1}, $\nu_2(^{37}Cl) = 1183.217$ cm^{-1}), rotational and centrifugal distortion constants. The r_0 structure of $^{35}ClH_2^+$ was determined as : $r_{HCl} = 1.3135(87)$ Å and $HClH = 94.3(1\ 2)°$, which are in good agreement with ab inito calculation (1.306 Å, 94.9°) by Botschwina.[1]

[1]P. Botschwina, in Molecular Ions: Geometrical and Electronic Structures, edited by J. Berkowitz and K. Groeneveld (Plenum, New York, 1983).

Address: Institute for Molecular Science, Okazaki 444, Japan.

ME10.

INFRARED DIODE LASER SPECTROSCOPY OF THE HYDROGEN BIFLUORIDE ANION: FHF⁻ AND FDF⁻

K. KAWAGUCHI AND E. HIROTA

The ν_3 vibration-rotation transition of the hydrogen bifluoride anion($D_{\infty h}$) has been detected by infrared diode laser spectroscopy using the magnetic field modulation technique.[1] The anion was generated by a hollow cathode discharge in a mixture of H_2 and a fluorine-containing molecule such as CF_4, C_2F_4, and CHF_3. Carbon compound was indispensable to produce the anion.

Identification of the species was based on the spectral pattern showing intensity alternation, the magnitude of the rotational constant ($B'' = 0.334181$ cm^{-1}) and the ion drift velocity sign determined by the velocity modulation method. The observed ν_3 frequencies of FHF⁻ (1848.699 cm^{-1}) and FDF⁻ (1397.236 cm^{-1}) are much different from the reported values $(\nu_3 = 1284-1563$ cm$^{-1})$ in the solid phase. In contrast, the ν_1 (617 cm^{-1}) and ν_2 (1241 cm^{-1}) frequencies estimated from the centrifugal distortion constant and the energy difference between the $\nu_1 + \nu_2$ and ν_3 states derived from an analysis of Coriolis perturbation are in good agreement with solid state measurements. The F-F bond length in FHF⁻ derived from the B'' value is $r_0 = 2.304\,432(52)$ Å, which is longer than the solid phase length (2.277(6) Å in KHF_2 and 2.264(3) Å in N_aHF_2).

[1] K. Kawaguchi, C. Yamada, S. Saito, and E. Hirota, J. Chem. Phys. 82, 1750 (1985).

Address: Institute for Molecular Science, Okazaki 444, Japan.

ME11.

CALCULATED SPECTROSCOPIC PROPERTIES OF HBF⁺ AND HBCL⁺

P. BOTSCHWINA

Potential surfaces and various spectroscopic properties (vibrational frequencies, IR intensities, dipole moment functions, rotational constants, centrifugal distortion constants, and rotation-vibration constants) have been calculated for HBF⁺ and HBCl⁺ from highly correlated CEPA wavefunctions. The results for HBF⁺ are in excellent agreement with a recent laser IR investigation of the ν_3 band.[1] The ν_3 bands of both ions are quite strong and the ν_1 bands are rather weak. The less stable isomers HFB⁺ and HClB⁺ are also discussed.

[1] K. Kawaguchi and E. Hirota, Chem. Phys. Letters 123, 1(1986).

Adress: Fachbereich Chemie der Universität Kaiserslautern, D-6750 Kaiserslautern, West Germany

ME12. (4:28)

CALCULATED SPECTROSCOPIC PROPERTIES OF SOME SMALL POLYATOMIC ANIONS

P. BOTSCHWINA

Near-equilibrium potential surfaces have been calculated for the electronic ground states of the anions NH_2^-, PH_2^-, AsH_2^-, HCC^-, HO_2^-, N_3^-, and HCO_2^- from highly correlated CEPA wavefunctions. Anharmonic vibrational frequencies and IR intensities have been computed and other spectroscopic properties such as rotational constants, centrifugal distortion constants and rotation-vibration coupling constants are reported.

Adress: Fachbereich Chemie der Universität Kaiserslautern, D-6750 Kaiserslautern, West Germany

ME13. (4:45)

THE INFRARED SPECTRUM AND NORMAL COORDINATE ANALYSIS OF THE BICARBONATE ION

Howard Coker and William Kearney

Solid solutions of the bicarbonate ion in alkali halide single crystals give spectra superior to these obtained by previous investigators using alkali halide pellets. The bicarbonate ion has been isolated in single crystals by diffusion and by the reaction of water with carbonate ion in carbonate-doped crystals. The conversion of carbonate to bicarbonate is only partial, and the reaction reverses at room temperature. However, quantitative and stable conversion is effected by heating the carbonate-doped crystals with both water vapor and carbon dioxide at temperatures sufficient for diffusion of carbon dioxide into the crystal. The carbon dioxide reacts with the hydroxide ion produced by the reaction $HOH + CO_3^= \rightarrow HCO_3^- + OH^-$. The method of Gwinn was used in a revised program for the calculation of a set of harmonic force constants.

Address of Coker: Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069
Address of Kearney: Department of Chemistry, University of Iowa, Iowa City, Iowa 52240

ME14. (4:57)

THE ν_2 BAND OF HOBr

E. A. COHEN AND G. A. McRAE

The ν_2 band of HOBr has been observed at $0.0056 cm^{-1}$ resolution using the McMath Solar Telescope Fourier transform spectrometer at Kitt Peak National Observatory. Although some difficulty was encountered generating the sample, transitions were assignable for Ka<5 and J<42. Coriolis resonances have been observed between the Ka=2 levels of ν_2 and the otherwise unobservable Ka=1 levels of $2\nu_3$. The spectrum will be described and molecular parameters for ν_2, $2\nu_3$ and their interaction will be presented.

Address of Cohen and McRae: Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109, USA

MF1. (1:30)

MEASURED RADIATIVE LIFETIMES FOR H_2 AND HD IN THE E,F $^1\Sigma_g^+$ ELECTRONIC STATE[*]

D. W. CHANDLER AND L. R. THORNE

We have used tunable, pulsed ultraviolet laser radiation to prepare H_2 and HD in selected rovibronic levels of the E,F $^1\Sigma_g^+$ electronic state. This state is accessible from the ground state, X $^1\Sigma_g^+$, by means of two-photon excitation. Subsequent absorption of near infrared laser radiation by molecules prepared in the E,F $^1\Sigma_g^+$ state produces ions that are detected by a time-of-flight mass spectrometer. Radiative lifetimes of individual rovibronic levels are determined by measuring the ion signal as a function of the time delay between the ultraviolet and near-infrared laser pulses. A decreasing exponential function is fit to the ion signal associated with a particular level to obtain its lifetime. Measured lifetimes are in good agreement with previously reported theoretical lifetimes. In addition, we have measured several lifetimes for which no theoretical values are available.

Address of Chandler and Thorne: Combustion Research Facility, Sandia National Laboratories, Livermore, California 94550.

MF2. (1:42)

SCHUMANN-RUNGE ABSORPTION BANDS OF $^{16}O^{18}O$

K. Yoshino, D.E. Freeman, and W.H. Parkinson

The absorption spectrum of the Schumann-Runge bands of isotopic oxygen, $^{16}O^{18}O$, has been investigated with a 6.65 m vacuum spectrograph in the wavelength region 175-198 nm. The absorption cell, 50 cm in length, can be cooled with liquid nitrogen. Most of bands are as diffuse as those of other isotopic molecules of oxygen. The diffuseness of absorption lines of the isotopes varies slightly and will be demonstrated. Rotational analyses have been completed for (16,0) through (2,0) bands.

Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138

MF3. (1:54)

HIGH RESOLUTION CROSS SECTIONS AND BAND OSCILLATOR STRENGTHS OF THE SCHUMANN-RUNGE BANDS OF ISOTOPIC OXYGEN

K. Yoshino, D.E. Freeman, J.R. Esmond, and W.H. Parkinson

Photoabsorption cross sections of isotopic oxygen, $^{16}O_2$, $^{18}O_2$, and $^{16}O^{18}O$, at 79K have been obtained from photoabsorption measurements at various pressures throughout the wavelength region 179-201 nm with a 6.65 m photoelectric scanning spectrometer. The absolute cross sections are obtained for the (12,0) through (2,0) bands of $^{16}O_2$, (14,0) through (2,0) bands, except for the (12,0) band, of $^{18}O_2$, and (13,0) through (3,0) bands of $^{16}O^{18}O$. Band oscillator strengths of these bands have been determined by direct numerical integration of the measured cross sections.

Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138

MF4.

AN ELECTRIC QUADRUPOLE TRANSITION: THE b $^1\Sigma_g^+$ - a $^1\Delta_g$ EMISSION SYSTEM OF OXYGEN

E.H. FINK, H. KRUSE, D.A. RAMSAY, AND M. VERVLOET

The 0-0 band of the b $^1\Sigma_g^+$ - a $^1\Delta_g$ system of oxygen near 5200 cm^{-1} has been recorded in emission using a Bomem Fourier transform spectrometer. Five branches are observed with $\Delta J = 0, \pm 1, \pm 2$. The relative intensities of the branches agree with those calculated for an electric quadrupole transition.

Address of Fink and Kruse: Physikalische Chemie-Fachbereich 9, Bergische Universität-Gesamthochschule Wuppertal, D-5600 Wuppertal 1, Federal Republic of Germany
Address of Ramsay and Vervloet: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR6

MF5.

NEAR-INFRARED EMISSION SPECTRA OF S_2 AND SeS

E.H. FINK, H. KRUSE, D.A. RAMSAY, AND D.C. WANG

Bands of the b $^1\Sigma_g^+$ - X $^3\Sigma_g^-$ system of S_2 have been excited in a discharge flow system by reacting ground state S_2 molecules with metastable O_2 ($^1\Delta_g$) molecules. The 0-0, 0-1 and 1-1 bands have been recorded in emission with a Bomem interferometer, together with the 0-0 band of $^{32}S^{34}S$. The rotational structures of the bands are determined by magnetic dipole selection rules. Detailed analysis has yielded accurate values for the molecular constants of the b $^1\Sigma_g^+$ and X $^3\Sigma_g^-$ states. The rotational line intensities are well reproduced by the line strength formulae of Watson.

Bands of the b 0^+ - X_1 0^+ and b 0^+ - X_2 1 systems of SeS have been excited in a similar manner. In the 0-0 band, four electric dipole and three magnetic dipole branches have been found. Relative magnitudes of the two electric dipole and one magnetic dipole transition moments have been determined. Molecular constants have been determined for the five isotopic species ^{80}SeS, ^{78}SeS, ^{82}SeS, ^{76}SeS and ^{77}SeS.

[1]J.K.G. Watson, Can. J. Phys. 46, 1637 (1968).

Address of Fink and Kruse: Physikalische Chemie-Fachbereich 9, Bergische Universität-Gesamthochschule Wuppertal, D-5600 Wuppertal 1, Federal Republic of Germany
Address of Ramsay and Wang*: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR6

*(Visiting Scientist) Permanent Address: Physics Department, Yunnan University, Kunming, Yunnan Province, People's Republic of China

MF6. (2:35)

REINVESTIGATION OF THE E,F ← X SYSTEMS OF S_2

C. G. Mahajan

The absorption spectrum of S_2 in the region 140-152 nm has been reinvestigated by taking fourth order spectra on a 6-meter normal incidence spectrograph and using 'afterglow' technique with the Lyman-type flash as background source.

A comparison of the present high resolution spectra (though a rotational analysis has not yet been carried out) with the earlier studies[1,2] has revealed the following differences;

(i) No doublet structure is observed except for the relatively weak bands designated as (0,0) and (1,0) of E ← X and F ← X systems, respectively, indicating that the bands forming doublet structure in the earlier studies may possibly belong to another system.

(ii) Contrary to the E ← X system, the observed components of (1,0), (2,0) and (3,0) bands of the F ← X system are clearly red degraded (i.e. $r'_e > r''_e$, and hence weakening of bonding strength) whereas the (0,0) band does not show any clear degradation. Further, the rotational structure of the (2,0) band appears to be different from those of the (1,0) and (3,0) bands suggesting that it may not belong to the progression.

(iii) No band with appreciable intensity is observed below 144 nm. In view of the above it is tentatively assumed that the states arising from the configuration....$(\pi_g 3p)(\pi_u 5p)$ may still be approximating to Russell-Saunders coupling.

1. R. J. Donovan, D. Husain and C. D. Stevenson, Trans. Faraday Soc., 66, 1 (1970).
2. C. G. Mahajan, G. Lakshmi Narayana and N. A. Narasimham, Ind. J. Pure Appl. Phys., 14, 488 (1976).

Address of Mahajan: Department of Physics, Panjab University, Chandigarh -- 160014, India; now at Department of Physics, University of Toronto, Toronto, Ontario, Canada, M5S 1A7.

MF7. (3:00)

HIGH RESOLUTION FOURIER TRANSFORM EMISSION SPECTROSCOPY OF CP AND PH

R.S. RAM AND P.F. BERNATH

The vibration-rotation spectrum of PH and the $A^2\Pi$-$X^2\Sigma^+$ electronic transition of CP were recorded in the infrared with the Fourier transform spectrometer associated with the McMath Solar Telescope at Kitt Peak.

CP and PH were made in a microwave discharge of P_4 vapor and H_2. The carbon required to make CP was present as a deposit on the discharge tube walls. The 1-0, 2-1 and 3-2 and 4-3 vibration-rotation bands of the $X^3\Sigma^-$ state of PH were observed and molecular constants extracted. For CP the 0-0, 1-0, 3-1, 0-1, 0-2 bands of the $A^2\Pi$-$X^2\Sigma^+$ transition were observed from 4000-8600cm^{-1}. The A-X transition of CP is analogous to the red system of CN.

Address of Ram and Bernath: Department of Chemistry, University of Arizona, Tucson, Arizona 85721.

MF8. (3:17)

ROTATIONAL LINE INTENSITIES IN THE $b^1\Sigma^+ - X^3\Sigma^-$ SYSTEM OF THE NF MOLECULE

M. VERVLOET AND J. K. G. WATSON

The 0-0 band of the $b^1\Sigma^+ - X^3\Sigma^-$ electronic transition of the NF molecule[1] has been recorded with a Bomem Fourier transform spectrometer and the rotational line intensities have been fitted to theoretical formulas[2] involving both parallel (μ_0) and perpendicular (μ_1) transition moments. The value obtained for the ratio μ_1/μ_0 is 0.261, with standard deviation 0.004. This result, which corrects previous misstatements in Refs. 1 and 2 that the perpendicular component is stronger, can be combined with measured radiative lifetimes[3] to give experimental values of μ_0 and μ_1 that will be compared with ab initio values[4,5].

[1] A. E. Douglas and W. E. Jones, Can. J. Phys. **44**, 2251 (1966).
[2] J. K. G. Watson, Can. J. Phys. **46**, 1637 (1968).
[3] P. H. Tennyson, A. Fontijn, and M. A. A. Clyne, Chem. Phys. **62**, 171 (1981).
[4] F. D. Wayne and E. A. Colbourn, Mol. Phys. **34**, 1141 (1977); **51**, 531 (1984).
[5] S. J. Havriliak and D. R. Yarkony, J. Chem. Phys. **83**, 1168 (1985).

Address of Vervloet and Watson: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

MF9. (3:29)

RADIATIVE LIFETIMES OF THE 0_u^- SUBLEVELS OF THE RARE GAS EXCIMERS[*]

DAVID L. HUESTIS

Some years ago[1] we studied the structure of the low lying excited states of the rare gas excimers using a simple model hamiltonian based on parameterized quantities called the Σ-Π, spin-orbit, and singlet-triplet splittings. We were also able to estimate radiative lifetimes of the the 1_u sublevel of the $^3\Sigma_u^+$ state, which where used to select among the available experimental data, yielding values of 5, 3, 0.3, and 0.1 µsec for Ne_2^*, Ar_2^*, Kr_2^*, and Xe_2^* respectively.

In subsequent kinetic studies the third component of the $^3\Sigma_u^+$ state, designated 0_u^-, has been supposed either to be entirely metastable, or has been otherwise ignored. In the present investigation we expand our previous model hamiltonian to include rotational coupling among the $^{1,3}\Sigma_u^+$ and $^{1,3}\Pi_u$ states. We find that for all four Rg_2^* species the thermally averaged radiative lifetime of the 0_u^- sublevel should be between 2 and 10 µsec. In the case of Ne_2^*, which is well described by Hund's case (b) the lifetime is nearly independent of J (the F_1 and F_3 components have lifetimes about twice that of F_2). While for Xe_2^*, which is essentially case (c), the lifetime varies inversely with $J(J+1)$ ($\tau_1 \gg \tau_3 \approx \tau_2$).

In high-pressure gas experiments, collisional mixing of the three triplet components would probably prevent their separate observation. In a beam experiment, the low-J levels of Xe_2^* 0_u^- would be quite long lived, and the total population would decay non-exponentially.

[1] D. C. Lorents, D. J. Eckstrom, D. L. Huestis, SRI International Report No. MP 73-2 (1973).

Address of Author: Chemical Physics Laboratory, SRI International, Menlo Park, CA 94025

MF10. (3:46)

HIGH-RESOLUTION VUV LASER-EXCITED SPECTRA OF Ar_2

P. R. Herman and B. P. Stoicheff

Tunable, coherent, and monochromatic radiation, generated by four-wave sum-mixing in Hg vapor[1] was used to investigate spectra of Ar_2 in the region 104 - 108 nm. Argon dimers were formed by pulsed supersonic expansion, and rovibronic transitions were detected by fluorescence emission[2] and by photo-ionization. A comprehensive study of high-resolution spectra, corresponding to transitions from the van der Waals ground state to the three lowest excimer states was carried out, resulting in new information on spectroscopic constants.

The observation of isotopic spectra of $^{40}Ar_2$ and $^{36}Ar\ ^{40}Ar$ has led to unambiguous vibrational numbering and to vibrational constants for the A and B states for the first time. Analyses of rovibronic structures have yielded new and improved[3] rotational constants and internuclear distances. These data have been used to calculate potential energy curves for the excited states of Ar_2. At a resolving power $>5 \times 10^5$, three branches were observed in the band system A - X, revealing Ω-type doubling of rotational levels of the A state. This has firmly established Hund's coupling case (c) and the symmetry 1_u for the A state.

A brief description of the experimental technique will be presented along with the spectroscopic results.

1. P. R. Herman and B. P. Stoicheff, Opt. Lett. 10, 502 (1985).
2. R. H. Lipson, P. E. LaRocque, and B. P. Stoicheff, J. Chem. Phys. 82, 4470 (1985).
3. E. A. Colbourn and A. E. Douglas, J. Chem. Phys. 65, 1741 (1976); D. E. Freeman,
    K. Yoshino, and Y. Tanaka, J. Chem. Phys. 71, 1780 (1979).

Address of Herman and Stoicheff: Department of Physics, University of Toronto, Toronto, Ontario, Canada, M5S 1A7.

MF11. (4:03)

THE $B^2\Sigma^+-X^2\Sigma^+$ SYSTEM OF $^{12}C^{16}O^+$ AND $^{13}C^{16}O^+$

P. MISRA, C. WELDON MATHEWS, D. W. FERGUSON, AND K. NARAHARI RAO

A 10-meter Czerny-Turner infrared spectrometer has been modified and adapted into an instrument with a 50 cm focal plane suitable for photographic recording of spectra between about 1800 and 8000 Angstroms. The 20 cm x 40 cm Bausch and Lomb plane grating used in the Czerny-Turner system has been precisely calibrated employing several standard wavelengths. The emission spectrum of CO^+ has provided a good test for the resolution of the remodeled spectrograph in the ultraviolet.

A hollow cathode discharge lamp has been employed to generate the 0-0, 0-1, and 0-2 bands of the $B^2\Sigma^+-X^2\Sigma^+$ system of $^{12}C^{16}O^+$ and $^{13}C^{16}O^+$ in emission. A nonlinear least-squares fitting routine has been used to analyze the bands. In the case of $^{12}C^{16}O^+$, current data have been analyzed taking full advantage of available microwave data for the ground state, thereby permitting comparisons with previous results. Results of the study on $^{13}C^{16}O^+$ provide the first determination of molecular constants for this isotopic species in the $B^2\Sigma^+$ and the $X^2\Sigma^+$ electronic states.

Address of Misra, Ferguson and Rao: Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

Address of Mathews: Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

MF12. (4:15)

ZEEMAN SPLITTING OF THE $A^1\Sigma_u^+ \sim b^3\Pi_u$ PERTURBED LEVELS OF $^6Li_2$

R. A. BERNHEIM, L. P. GOLD, W-H. JENG, AND X. XIE

The $^6Li_2$ $A^1\Sigma_u^+$ (v=2, J=33) level is spin-orbit perturbed by the $b^3\Pi_u$ (v=9, F_{1e}, N=32) level.[1] We have studied the effects of magnetic fields up to 5 kG on these perturbed levels using magnetic rotation spectroscopy and sub-Doppler polarization spectroscopy to observe the zero-field separation, Zeeman splittings, and intensity changes of the $(A^1\Sigma_u^+; b^3\Pi_u) \leftarrow X^1\Sigma_g^+$ spectra. Different M components were selectively observed with different orientations of the magnetic field relative to the laser polarization.

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[1]X. Xie and R. W. Field, Chem. Phys. 99, 337 (1985).

Address: Department of Chemistry, Davey Laboratory, The Pennsylvania State University, University Park, PA 16802.

MF13. (4:32)

FLUORESCENCE QUENCHING IN THE $B^3\Sigma_{0^+u} \sim b^3\Pi_u$ PERTURBED LEVELS OF $^6Li_2$

B. R. REDDY and S. PADDI REDDY

Fluorescence in the $B^3\Pi_{0^+u} - X^1\Sigma_g^+$ system of I_2 excited with a tunable single-frequency dye laser was recorded photoelectrically for pure iodine and iodine-foreign gas mixtures. From the measured relative intensities, energy transfer efficiencies for $\Delta v' = \pm 1$ as well as the self and foreign gas quenching efficiencies have been determined for several vibrational and rotational levels of state B. From these studies, the v, J level of B at which one of the repulsive electronic states crosses is also estimated.

Address: Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland, Canada. A1B 3X7

MF14. (4:49)

Emission Spectroscopy of IF $A^3\Pi(1)$: Medium Resolution Vibrational Analysis

B. D. McFeeters and P. J. Wolf

Chemiluminescence emission has been observed from IF in a flow of I_2 and F_2 at a cell temperature of 400°C. Spectra have been recorded under medium resolution from 470 to 750 nm, and structure originating from the $A^3\Pi(1)$ state and terminating in the ground, $X\Sigma^+$ state has been observed. Bandheads in progressions based on $0 \leq v' \leq 15$ and $0 \leq v'' \leq 5$ have been measured and assigned. A new vibrational numbering for the A state is proposed which leads to improved molecular constants: $T_e = (14936\pm2)cm^{-1}$, $\omega_e = (386.3 \pm 0.8)cm^{-1}$, $\omega_e x_e = (2.51 \pm 0.11)$ cm^{-1}, $\omega_e z_e = (- 0.056 \pm 0.005)$ cm^{-1}, $D_e = (7884 \pm 300)$ cm^{-1}.

The IF(A) emission showed a strong dependence on cell temperature with the most prominent features appearing at 400-500°C. These results are explained on the basis of the rapidity of electronic quenching at the lower cell temperatures.

Address of McFeeters: Advanced Chemical Laser Branch, Air Force Weapons Laboratory, Kirtland AFB, New Mexico 87117-6008.

Address of Wolf: Defense Nuclear Agency, Shock Physics and Aerospace Systems, Washington, D.C. 20305-1000

MG1. (1:30)

MOLECULAR PARAMETERS FOR CARBON DIOXIDE ABSORPTIONS IN THE 3450 cm^{-1} SPECTRAL REGION

D. CHRIS BENNER, V. MALATHY DEVI AND CURTIS P. RINSLAND

Line positions and intensities of carbon dioxide transitions between 3400 and about 3500 cm^{-1} have been determined from long-path, low-pressure, room-temperature spectra recorded with 0.01 cm^{-1} resolution using the Fourier transform spectrometer in the McMath telescope of the National Solar Observatory. Numerous vibration-rotation bands have been identified. The upper level of the $(21^11)_{III} - (11^10)_I$ band interacts with the $(40^00)_{II}$ vibrational level.

A non-linear least squares spectral fitting technique has been applied to all unblended CO_2 lines in these spectra. The pressure ranged from 1 to 10 Torr with an absorption path of up to 385 m. The measured intensities have been analyzed to determine vibrational band intensities and F-factor coefficients for the bands not extending beyond our high frequency limit.

Address of Benner and Malathy Devi: Department of Physics, College of William and Mary, Williamsburg, VA 23185
Address of Rinsland: NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23665

MG2. (1:37)

SENSITIVITY OF BAND INTENSITIES OF CO$_2$ TO EXPERIMENTAL DATA IN DIRECT NUMERICAL DIAGONALIZATION CALCULATIONS

RICHARD B. WATTSON and LAURENCE S. ROTHMAN

Calculations of band intensities for parallel bands of the symmetric species of carbon dioxide have been carried out[1]. The method employed, Direct Numerical Diagonalization, has been discussed at previous Ohio State Symposia. The significance of the choice of data used to determine the dipole moment function will be presented. The values of band intensities predicted by the method are primarily influenced by transitions from the ground state. Some observed bands from different spectral regions are strongly coupled, whereas other combinations of bands have been found to be loosely coupled. The data that are strongly coupled will be presented as an example to aid experimentalists in correlating their observations with other groups with respect to absolute errors.

The recent results[1] for parallel band intensities have also been augmented by perpendicular band intensity calculations.

1. R. B. Wattson and L. S. Rothman, submitted to J. Mol. Spectrosc. (1986).

Address of Wattson: Visidyne, Inc., 10 Corporate Place, S. Bedford St., Burlington, MA 01803
Address of Rothman: Optics Division, Air Force Geophysics Laboratory, Hanscom AFB, MA 01731

MG3.

THE NEW VERSION OF THE HITRAN DATABASE: EXAMPLE OF CARBON DIOXIDE LINE PARAMETERS

LAURENCE S. ROTHMAN, RICHARD B. WATTSON, and ROBERT R. GAMACHE

A new version of the atmospheric absorption line parameter compilation (HITRAN database) has been implemented. The data that have been archived in the versions prior to this time have consisted of a minimal set of four fundamental parameters for each discrete line transition above a chosen threshold required for calculations of atmospheric transmission and radiance[1]. The structure of the database has been expanded to allow for additional molecular parameters, such as self-broadened linewidths, temperature dependence of halfwidths, line shifts, and transition moments, that extend the capabilities to upper atmospheric comparisons and to satisfy proposed satellite experimental techniques.
Major updates of the parameters have occurred; the specific case of CO_2 will be presented. Major improvement has been effected by new line position calculations and the assimilation of recent laboratory measurements of intensities[2] as well as the new theoretical treatment of parallel band intensities[3] and recent linewidth measurements[4].

1. L. S. Rothman et al, Appl. Opt. 22, 2247-2256(1983); 22, 1616-1627(1983).
2. L. S. Rothman, Appl. Opt. 26,   (1986).
3. R. B. Wattson and L. S. Rothman, submitted to J. Mol. Spectrosc. (1986).
4. E. Arié, N. Lacome, Ph. Arcas, and A. Levy, Appl. Opt., in press(1986).

Address of Rothman: Optics Division, Air Force Geophysics Laboratory,
                    Hanscom AFB, MA 01731
Address of Wattson: Visidyne, Inc., 10 Corporate Place, S. Bedford St.,
                    Burlington, MA 01803
Address of Gamache: University of Lowell Center for Atmospheric Research,
                    450 Aiken St., Lowell, MA 01854

MG4.

LINE POSITIONS AND LINE STRENGTHS OF CO_2 BANDS IN THE 750 TO 1100 CM^{-1} REGION

L.R. BROWN

The line positions and line strengths of $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{16}O^{18}O$ have been measured in spectra recorded at 0.0056 cm^{-1} resolution (unapodized) using the Fourier transform spectrometer located at the McMath telescope at Kitt Peak National Observatory. Lines with strengths between 1×10^{-2} $cm^{-2}.atm^{-1}$ and 1×10^{-5} $cm^{-2}.atm^{-1}$ have been analyzed with precisions of 3×10^{-5} cm^{-1} to 4×10^{-4} cm^{-1} for line positions and 3% to 10% for line strengths, depending on the strength of the line. Some two dozen bands have been fitted for rotational constants and band strengths.

Address: Jet Propulsion Laboratory, Mailstop 183-301, 4800 Oak Grove Drive, Pasadena, CA 91109

MG5.

LINE POSITIONS OF $\Delta v_3 = 1$ BANDS OF $^{12}C^{16}O^{18}O$

MARK P. ESPLIN AND JOHN P. MYCROFT

Spectra of a CO_2 sample enriched with ^{18}O have been measured using a 3.5 m path high temperature absorption cell and the AFGL high resolution interferometer. The spectra were taken at a resolution of 0.007 cm^{-1}, at temperatures of 300, 500, and 800 K, and pressures of 3 and 6 torr. Ten $\Delta v_3 = 1$ bands have been identified previously in the experimental spectra and molecular constants for these bands have been reported.[1] Further analysis of these spectra has resulted in the identification of additional bands. Effective rotation-vibration constants for these bands will be presented.

[1] M. P. Esplin and L. S. Rothman, J. Mol. Spectrosc. 100, 193-204 (1983).

Address of Esplin: Stewart Radiance Laboratory, Utah State University, 139 The Great Rd., Bedford MA 01730.

Address of Mycroft: Geophysics Scholar, Optical Physics Division, U. S. Air Force Geophysics Laboratory, Hanscom AFB, MA 01731.

MG6.

THE LASER QUANTITATIVE SPECTRA OF DIOXIDE CARBON AT 10μ BANDS

CAI PEIPEI, SHEN SHANXIONG, ZHANG HANSHENG, AND I-SHAN ZHENG

Recent measuring of CO_2 vi-rotational lines at 10μ bands has performed under the temperature dependent conditions, ranging from room temperature to around hundreds. The line strength, half-width due pressure broadening and its temperature dependent factors have been obtained through experiments. The results showed that the theoretical calculating values of atmospheric absorption for laser radiation were strongly dependent on atmosphere temperature since the spectra dependence of the cross section varied at different conditions. The data given referred to a wide range of quantitative spectral parameters, including line strength, self and N_2-broadening.

Address: Department of Physics, East-China Normal University, Shanghai, 200062, People's Republic of China

MG'1.   (2:45)

VIBRATIONAL ASSIGNMENTS OF BANDS RESOLVED BY LOW TEMPERATURE, MATRIX ISOLATION
TECHNIQUES

D. Presser, F.M. Wasacz, and R.J. Jakobsen

In the course of using the Mattson Cryolect to obtain low temperature, matrix isolation reference spectra; it was observed that the combination of the low temperature and the use of the matrix isolation technique resolved an unusually large number of infrared peaks especially in the CH stretching region. This preliminary work describes the efforts to relate this infrared bands to molecular structural features and to determine the nature of the vibrations.

Combination and overtone bands as well as crystal field splitting were considered and the relation to structural features was supported by the use of deuterated molecules. This relation to structural feature has demonstrated that the "extra" bands produced by this technique can be used to identify structural groups of molecules as well as elucidate molecular geometry.

Address of Presser and Wasacz: Mattson Instruments, Inc., 6333 Odana Road, Madison, Wisconsin 53719

Address of Jakobsen: Mattson Institute for Spectroscopic Research, 326 Walhalla Road, Columbus, Ohio 43202

MG'2.   (3:02)

EMISSION SPECTRA FOR MATRIX ISOLATED IF:
OBSERVATION OF A NEW LOW LYING ELECTRONIC STATE

J.P. NICOLAÏ and M.C. HEAVEN

Laser induced fluorescence spectroscopy of IF isolated in an Argon matrix at 12K has been investigated. Following laser excitation at 355 nm, long-lived emission is observed in the near infra-red region. This emission, resolved with a monochromator, shows a vibrational progression at wavelengths of 721 nm up to 1333 nm. Spectral analysis indicates that the emission comes from the lowest vibrational level of a new low lying electronic state and terminates on the vibrational levels $v''=12$ up to $v''=25$ of the ground state $(X\ ^1\Sigma^+)$. This analysis provides an estimate for Te of about 20,800 cm^{-1} and an approximate equilibrium distance of 2.5 Å. The lifetime for this emission was also measured and found to be 7 msec. Details of these experiments and a possible assignment for this new low lying electronic state will be presented.

Address of Nicolaï and Heaven: Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616.

MG'3.   (3:19)

COMPARISON OF THE ELECTRONIC ENERGY LEVELS OF DIATOMIC MOLECULES IN THE GAS PHASE AND IN
INERT SOLID MATRICES

MARILYN E. JACOX

Electronic band origins and vibrational band spacings in excited electronic states have
been compared for the approximately 230 electronic transitions of diatomic molecules which
have been observed both in the gas phase and in rare-gas or nitrogen matrices. With few ex-
ceptions, valence transitions and the associated vibrational band spacings are shifted by
less than about 1% in neon matrices. Somewhat larger shifts, often to longer wavelengths,
result from isolation of the molecule in a heavier rare-gas or a nitrogen matrix. The per-
turbation of Rydberg transitions by the matrix and the effects of charge-transfer inter-
action with the matrix will be discussed.

Address: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

MG'4.   (3:36)

THE A $^2\Pi$ - X $^2\Sigma^+$ NEAR INFRARED ABSORPTION SPECTRUM OF HC_2 ISOLATED IN SOLID ARGON

MARILYN E. JACOX

A consistently good yield of the HC_2 free radical has been obtained when an $Ar:C_2H_2$ mix-
ture is codeposited at 12-14 K with a beam of argon atoms excited in a microwave discharge.
Using these conditions and the DA3.002 interferometer operated at 0.2 cm^{-1} resolution, the
A $^2\Pi$ - X $^2\Sigma^+$ band system of HC_2[1,2] has been observed in absorption between 3800 and 7500 cm^{-1}.
Detailed observations of the carbon-13 and deuterium-substituted species of HC_2, which have
yielded information on the position of the band origin and on the vibrational energy levels
of both the ground and the excited electronic state, will be considered.

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[1]P. G. Carrick, A. J. Merer, and R. F. Curl, Jr., J. Chem. Phys. 78, 3652 (1983).

[2]R. F. Curl, P. G. Carrick, and A. J. Merer, J. Chem. Phys. 82, 3479 (1985).

Address: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

COLOR CENTER LASER SPECTROSCOPY OF C_2D AND C_2H

Y-B. Yan, C. B. Dane, Jeffrey L. Hall, and R. F. Curl

The infrared spectrum of a discharge in argon over d-polyacetylene has been obtained using a color center laser spectrometer and magnetic rotation detection. Many lines (~3-5 per cm^{-1}) are observed, some of which can be identified as Ar atom transitions or as lines of the Ballik-Ramsay bands of C_2. In particular, two bands of the $\tilde{A}^2\Pi \leftarrow \tilde{X}^2\Sigma^+$ electronic transition of C_2D have been identified, assigned, and analyzed. One near 3730 cm^{-1} is a hot band of the bending mode of vibronic symmetry type $^2\Sigma^- \leftarrow ^2\Pi$. The other near 3850 cm^{-1} is of $^2\Pi \leftarrow ^2\Sigma^+$ symmetry involving the ground vibronic state of the molecule.

Five bands of C_2H had been previously observed[1] in this system by these methods and analyzed[2]. Four are of the type, $^2\Pi \leftarrow ^2\Sigma^+$ with the lower state the ground vibronic state of the molecule, and the fifth is a hot band of vibronic symmetry $^2\Sigma^- \leftarrow ^2\Pi$. A new band near 3600 cm^{-1} in C_2H has been assigned and analyzed. It is a $^2\Pi \leftarrow ^2\Sigma^+$ band involving the ground vibronic state (like four of the five older bands). Vibronic assignments for all the bands (C_2H and C_2D) will be proposed and the implications for the vibrational frequencies of C_2H will be discussed.

[1]P. G. Carrick, A. J. Merer, and R. F. Curl, J. Chem. Phys. **78**, 3652 (1983).

[2]R. F. Curl, P. G. Carrick, and A. J. Merer, J. Chem. Phys. **82**, 3479 (1985).

Address: Chemistry Department and Rice Quantum Institute, Rice University, Houston, Texas 77251, USA.

FTIR ISOTOPIC STUDY OF C_2H IN AN ARGON MATRIX

RICHARD A. SHEPHERD AND W.R.M. GRAHAM

An extensive FTIR isotopic study using deuterium and carbon-13 substitutions has been made on the vacuum uv photolysis products of acetylene trapped in argon matrices at 8 K. Absorption bands have been observed corresponding to several vibronic bands of the $A^2\pi \leftarrow X^2\Sigma$ transition of C_2H, which have recently been reported in studies on this radical using color center laser spectroscopy[1-2]. Isotopic shifts are reported for these bands as well as others attributed to C_2H.

The behavior of the band at 1846 cm^{-1} on isotopic substitution, is consistent with its previous assignment by Jacox[3] to the ν_3, C-C stretching vibration; however, the effects of carbon-13 substitutions on the band at 3610 cm^{-1} do not support its earlier assignment to the ν_1, C-H stretching vibration. Isotopic data on an absorption at 2104 cm^{-1} suggest that it may be a $\nu_2 + \nu_3$ combination band, which would imply an unexpectedly low value of ~260 cm^{-1} for the ν_2 bending vibration.

[1]P.G. Carrick, A.J. Merer, and R.F. Curl Jr., J. Chem. Phys. **78**, 3652 (1983).

[2]R.F. Curl, P.G. Carrick, and A.G. Merer, J. Chem. Phys. **82**, 3479 (1985).

[3]M.E. Jacox, Chem. Phys. **7**, 424 (1975).

Address of Shepherd and Graham: Department of Physics, Texas Christian University, Fort Worth, Texas 76129.

MG'7.   (4:27)

HYPERFINE AND QUADRUPOLE PARAMETERS OF THE MnH MOLECULE

R. J. VAN ZEE, D. A. GARLAND, and W. WELTNER, JR.

Using the double resonance technique of ENDOR, hyperfine and quadrupole coupling parameters have been obtained for the $X^7\Sigma$ electronic state of the $^{55}Mn^1H$ molecule isolated in solid argon at 4°K. From pumping the $M_S = \pm 1 \leftrightarrow 0$, $M_I = \pm 5/2$ or $\pm 3/2$ ESR lines, absorptions were observed from ΔM_I transitions within the $M_S = 0$ and ± 1 levels. From these frequencies an improved $A_\parallel(^{55}Mn)$ was derived and values for Q', the nuclear electric quadrupole parameter, and the ^1H hyperfine parameter, a_H, were derived. Combining information from ESR spectra[1] with that from ENDOR yields the following: $g_\perp = 2.000(1)$, $A_\parallel(^{55}Mn) = 334(6)$ MHz, $A_\perp(^{55}Mn) = 300(3)$ MHz, $Q'(^{55}Mn) = -11.81(2)$ MHz, $|a_H| = 6.8(1)$ MHz, $b_2^o = D = -0.003$ cm^{-1}.

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[1] R. J. Van Zee, T. C. DeVore, J. L. Wilkerson, and W. Weltner, Jr., J. Chem. Phys. 69, 1869 (1978).

Address of authors: Department of Chemistry, University of Florida, Gainesville, FL, 32611.

MG'8.   (4:39)

GROUND STATES AND HYPERFINE PARAMETERS FOR SOME TRANSITION-METAL CARBIDE MOLECULES

J. J. BIANCHINI, R. J. VAN ZEE, AND W. WELTNER, JR.

$^{59}Co^{13}C$ and $^{51}V^{13}C$ have been identified as $X^2\Sigma$ molecules from ESR spectra of argon matrices at 4°K. Both metal and ^{13}C hyperfine splittings were observed. VC spectra are unusual and imply coupling to a very low lying excited state.

Other spectra, believed to be due to the dicarbide molecules, ScC_2, VC_2, CoC_2, and MnC_2 with spins S = 1/2, 3/2, 1/2, and 5/2, respectively, were observed; however, ^{13}C hyperfine splittings were not resolved. From this and other reasoning, it is probable that carbon is bound as a C_2 unit in the molecule.

Address of authors: Department of Chemistry, University of Florida, Gainesville, FL, 32611.

MG'9.   (4:51)

Production of Clusters by Pulsed Laser Vaporization and their Trapping in Rare Gas Matrices

M. Rasenen, L. A. Heinbrook and V. E. Bondybey

One of the techniques which led recent progress in studies of bare metal clusters utilizes laser vaporization. Typically, metal or other material is vaporized by a laser pulse in the presence of an inert carrier gas, usually helium, and the products of clustering in the cooling plasma are studied by LIF, TOF mass spectroscopy or some other suitable spectroscopic technique. In the present work, we combine the pulsed laser vaporization with matrix isolation by replacing the He carrier gas with condensible gas, usually neon, and condensing the products on a 4K substrate. The advantage of this technique is that the products of many pulses can be accumulated and subjected to a subsequent leisurely spectroscopic study. Preliminary experiments show that enrichments in relative cluster concentrations of more than an order of magnitude, when compared with conventionally deposited samples, are easily accomplished. By adding suitable reactants to the neon carrier gas, metal oxides, nitrides or carbides can also be generated and studied. Experiments of this nature combined with electronic or infrared absorption or emission spectroscopy offer perhaps the best hope for structural characterization of a large variety of cluster species.

Address: A.T.& T. Bell Laboratories, Murray Hill, NJ, 07974.

TA1.   (8:40)

TRICARBON OXIDE SULFIDE, O=C=C=C=S, REVISITED

M. WINNEWISSER AND F. HOLLAND

The five-atomic linear molecules carbon suboxide, O=C=C=C=O, tricarbon oxide sulfide, O=C=C=C=S, and carbon subsulfide, S=C=C=C=S, are of considerable interest for both spectroscopists and astronomers[1]. Carbon suboxide belongs to the exotic group of quasilinear molecules[1], while the microwave experiments of C_3OS revealed beyond doubt the spectrum of a linear molecule[1]. In the case of C_3OS a new high yield synthesis[2] allows high-resolution study in the infrared region. In order to provide precision data for the assignment of the forthcoming high-resolution infrared spectra we have measured the millimeter wave spectrum of C_3OS for molecules in various excited vibrational states. The results of these studies will be discussed within the framework of earlier studies of O=C=C=C=S and recent work on S=C=C=C=S[3].

[1] B.P. Winnewisser, "The Spectra, Structure, and Dynamics of Quasi-linear molecules with Four or More Atoms" in Molecular Spectroscopy: Modern Research, Vol. III., Academic Press (1985).
[2] H. Bock, R. Dammel and D. Jaculi, "O=C=C=C=S: Synthesis and PE Spectrum", to be published (1986).
[3] F. Holland, K.M.T. Yamada, M. Winnewisser, C. Jarman, and H.W. Kroto, "The High Resolution FTIR and Diode Laser Spectrum of Carbon Subsulphide, S=C=C=C=S", Ninth Colloquium on High Resolution Molecular Spectroscopy, Riccione, 16-20 September 1985, Poster E17.

Address of Winnewisser and Holland: Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-6300 Giessen, Federal Republic of Germany

TA2.   (8:57)

NEW METHODS IN STRUCTURE DETERMINATION UTILIZING GROUND STATE ROTATIONAL CONSTANTS

MARLIN D. HARMONY AND WILLIAM H. TAYLOR

A new method for the determination of molecular structures from ground state spectroscopic data for a minimal set of isotopic species has been developed. The scheme is based on Watson's theory[1] and utilizes scaled moments of inertia which are defined (for a particular axis) by

$$I_m^\rho = (2\rho - 1)I_0$$

where ρ is evaluated (once) from $\rho = I_s/I_0$. I_s is the moment of inertia of the parent isotopic species computed from a single complete set of r_s coordinates. Structures computed from the scaled moments (I_m^ρ) appear to be significantly better approximations of the r_e structures than are the conventional r_s structures. The method will be described and illustrated for very simple heavy-atom polyatomic molecules, and its extension to larger molecules will be discussed.

[1] J.K.G. Watson, J. Mol. Spectrosc. 48, 479 (1973).

Address of Harmony and Taylor: Department of Chemistry, University of Kansas, Lawrence, KS 66045

TA3. (9:14)

MICROWAVE SPECTRUM, STRUCTURE AND DIPOLE MOMENT OF METHYLENECYCLOPROPENE

W.H. TAYLOR, M.D. HARMONY, T.D. NORDEN AND S.W. STALEY

The microwave spectrum of the normal and two C^{13} isotopic species of methylenecyclopropene has been observed and analyzed. The unstable cross-conjugated hydrocarbon was prepared in a flow system by passing 2-bromomethylenecyclopropane through a heated column packed with potassium t-butoxide.[1] Stark effect measurements led to a molecular electric dipole moment of 1.88 ± 0.01 Debye, and the rotational constants yielded a heavy-atom structure as follows: $C_1C_2 = 1.323 \pm 0.003$, $C_1C_3 = 1.441 \pm 0.006$ and $C_3C_4 = 1.332 \pm 0.006$ Å. The structure is discussed and compared to that of cyclopropenone, which has been rederived from earlier data.[2]

[1]S.W. Staley and T.D. Norden, J. Am. Chem. Soc. 106, 3699 (1984).

[2]J.M. Pochan, J.E. Baldwin and W.H. Flygare, J. Am. Chem. Soc. 91, 1896 (1969).

Address of Taylor and Harmony: Department of Chemistry, University of Kansas, Lawrence, KS 66045

Address of Norden and Staley: Department of Chemistry, University of Nebraska, Lincoln, NE 68588

TA4. (9:31)

OXYGEN-17 QUADRUPOLE COUPLING IN OPF$_3$ BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

J. MATOS, K. W. HILLIG II, AND R. L. KUCZKOWSKI

The $J = 1 \leftarrow 0$ rotational transition in ^{17}OPF$_3$ was measured by a pulsed supersonic nozzle FTMW spectrometer. This gave $B = 4491.420(3)$ MHz and eqQ = $-3.73(10)$ MHz. The quadrupole coupling constant is consistent with substantial π-bond character in the phosphorus-oxygen bond based on the Townes & Dailey model.

Address: Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

TA5. (9:43)

THE MICROWAVE SPECTRUM AND CONFORMATION OF METHOXY OZONIDE ($H_3COCHOOCH_2O$)

M. SOLTIS LABARGE, H. KEUL, AND R. L. KUCZKOWSKI

The microwave spectrum of methoxy ozonide (3-methoxy-1,2,4-trioxolane) has been assigned. The ground state rotational constants for the parent species are: A=4815.375(4) MHz, B=2435.842(3) MHz and C=2336.66(4) MHz. Spectra have also been assigned for the three species singly deuterated on the ring as well as the 5,5-d$_2$ species, the 3,5,5-d$_3$ species and the OCD$_3$ species. For the trans-d$_1$ and the OCD$_3$ species only Q branch transitions have been assigned.

A least-squares fit of the structure to twenty-two inertial parameters including moments of inertia, A-C, and Kappa indicates an axial methoxy group oriented over the ring. The dihedral angle O_e-C-O-CH$_3$ is approximately 55° where O_e is the ether oxygen.

Address of LaBarge and Kuczkowski: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.
Address of Keul: Lehrstuhl für Textilchemie und Makromoleculare Chemie, der RWTH, Aachen, West Germany.

TA6.

THE MICROWAVE SPECTRUM OF BISOXIRANE <u>C. F. SU</u>, R. L. COOK, and
V. F. KALASINSKY

The microwave spectrum of bisoxirane has been studied. The b-type transition lines of the ground vibrational state have been assigned and analyzed. The spectroscopic constants (MHz) based on the measured ground state lines are

$A = 10998.190\pm0.005$,
$B = 2340.413\pm0.002$,
$C = 2126.237\pm0.002$,

$\Delta_J = 0.2693\times10^{-3}\pm0.2894\times10^{-5}$,
$\Delta_{JK} = 0.2371\times10^{-3}\pm0.2288\times10^{-4}$,
$\Delta_K = 0.6835\times10^{-2}\pm0.5379\times10^{-3}$,
$\delta_K = 0.2028\times10^{-4}\pm0.2545\times10^{-6}$,
$\delta_K = 0.5254\times10^{-3}\pm0.3389\times10^{-4}$.

Several excited vibrational states have also been observed. The conformations of this molecule will be discussed and the microwave results will be compared with the electron diffraction and infrared results.

Address of Su and Cook: Department of Physics and Astronomy, Mississippi State University, Drawer 5167, Mississippi State, MS 39762.

Address of Kalasinsky: Department of Chemistry, Mississippi State University, Mississippi State, MS 39762.

TA7.

THE MILLIMETER AND SUBMILLIMETER WAVE SPECTRA OF CF^+ AND H_3O^+

GRANT M. PLUMMER, <u>TODD ANDERSON</u>, ERIC HERBST, AND FRANK C. DE LUCIA

We have used the magnetically enhanced negative glow discharge technique that we have previously described to study the millimeter and submillimeter wave spectra of CF^+ and H_3O^+. The CF^+ was detected in the discharge products of CF_4 and H_2 and the H_3O^+ in the discharge products of H_2 and O_2. For both of these species, either the precursor gases or intermediaries could be trapped at liquid nitrogen temperatures and the interaction of temperature, gas mixture, and observed spectra will be discussed. Observed frequencies and spectral constants will also be given.

<u>Address of Plummer, Anderson, Herbst, and De Lucia</u>: Department of Physics, Duke University, Durham, NC 27706

TA8. (10:42)

FREQUENCY TUNABILITY IN A SMALL OPTICALLY PUMPED FAR INFRARED LASER

HENRY EVERITT AND FRANK C. DE LUCIA

The tunability of a small, relatively high pressure optically pumped FIR laser has been studied. The laser cavity for this work was typically a circular waveguide 5 cm in length and 1/4 cm in radius. The laser frequency was tuned by adjustment of the cavity length via a plunger in one end of the waveguide. Pump radiation was coupled in and FIR radiation was emitted through a small iris in the other end of the waveguide cavity. The frequency of the laser was measured by mixing it with the signal from a millimeter/submillimeter spectrometer in an 1.5 K InSb detector. In a very simple system, tunabilities that approach 100 MHz have been observed for the 1.2 mm $^{13}CH_3F$ FIR laser. We believe that substantially wider tunablities can be achieved in an optimized system.

Address of Everitt and De Lucia: Department of Physics, Duke University, Durham, NC 27706

TA9. (10:59)

FREQUENCY MEASUREMENT OF FIR LASING TRANSITIONS

RICHARD L. CROWNOVER, DAVID D. SKATRUD, K.V.L.N. SASTRY, AND FRANK C. DE LUCIA

Millimeter and submillimeter spectroscopic techniques have been used to measure the frequencies, in absorption, of Far Infrared Laser transitions in a variety of molecules. The resulting values represent the laser frequencies unbiased by either pump offset or cavity pulling effects. In addition, pressure broadening parameters have been measured for a subset of the observed transitions.

Address of Crownover and De Lucia: Department of Physics, Duke University, Durham, NC 27706
Address of Skatrud: U.S. Army Research Office, Research Triangle Park, NC 27709
Address of Sastry: Department of Physics, University of New Brunswick, Fredericton, NB, E3B5A3

TA10. (11:16)

THE FAR INFRARED SPECTRA AND CONFORMATIONAL STABILITY OF 3-CHLOROPROPENE AND 3-CHLORO-2-METHYL-PROPENE

D. T. DURIG, T. S. LITTLE AND J. R. DURIG

The far infrared spectra of 3-chloropropene, CH_2CHCH_2Cl, and 3-chloro-2-methylpropene, $CH_2C(CH_3)CH_2Cl$, have been recorded, and the asymmetric torsions have been assigned for both the cis and gauche conformers. Hot bands have been observed on the low frequency side of the asymmetric torsional fundamentals and, from these data, the potential for internal rotation has been obtained. Values for the barriers to internal rotation and the ΔH between the conformers will be given.

Address: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

TA11. (11:33)

FAR INFRARED SPECTRA AND CONFORMATIONAL STABILITY OF FCH_2CFO, FCH_2CClO, AND FCH_2CBrO

H. PHAN, T. S. LITTLE, AND J. R. DURIG

The far infrared spectra of FCH_2CXO where X = F, Cl, and Br have been recorded, and the asymmetric torsional vibration has been identified for two conformers for each molecule. Each torsional transition shows a number of hot bands on the low frequency side of the fundamental. These transitions have been utilized to obtain the potential functions from which the barriers to internal rotation and the energy differences between the conformers have been obtained. Experimental values of the ΔH have also been obtained from the Raman spectra of each molecule as a function of temperature. These results will be compared to those obtained from ab initio calculations.

Address: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208..

TA12. (11:50)

MILLIMETER WAVE SPECTROSCOPY OF H - $\underset{..}{C}$ $\overset{..}{C}$ C - H ISOTOPOMERS
DETERMINATION OF THE r_s STRUCTURE

M. BOGEY, C. DEMUYNCK and J.L. DESTOMBES

A detailed analysis of the rotational spectrum of the reactive cyclopropenylidene C_3H_2 and of its isotopomers has been achieved.

C_3H_2, a ring molecule recently discovered by THADDEUS and coworkers [1] has been efficiently produced by a very weak R.F. discharge in allene C_3H_4. Fractionnal abundance as high as one percent has been obtained, allowing the ^{13}C substituted forms to be observed in natural abundance. The deuterated form has been created by adding small amounts of deuterium in the discharge.

From the rotational constants of the 4 studied species, it has been possible to derive a r_s structure, which is in very good agreement with recent ab initio calculations by LEE et al. [2].

(1) P. THADDEUS, J.M. VRTILEK and C.A. GOTTLIEB, Astrophys. J., 299, L 63 (1985).

(2) T.J. LEE, A. BUNGE and H.F. SCHAEFFER III, J. Am. Chem. Soc., 107, 137 (1985).

Address : Université de Lille I - Laboratoire de Spectroscopie Hertzienne associé au CNRS -
F 59655 Villeneuve d'Ascq Cedex - FRANCE

TB1   (8:30)

A LOW-TEMPERATURE ABSORPTION CELL FOR FTS AND DIODE LASER SPECTROSCOPY OF GASES

D. E. JENNINGS, G. W. HALSEY, AND J. J. HILLMAN

Laboratory spectroscopy of gases at reduced temperatures provides a means for simplifying complex spectra, narrowing doppler widths, assigning energy levels, and measuring line strengths and broadenings as functions of temperature. We have constructed a cell which can be operated at any temperature between 50 and 300 Kelvin. The cell has a 30-cm path with a 2.5-cm bore to permit multiple passing of a small laser beam. A unique feature of this design is that the windows are sealed to the cell with spring-loaded teflon o-rings, which have proven to maintain a good seal down to 50 Kelvin. The cell is cooled with a single-stage closed-cycle helium refrigerator and the cell is continuously variable in temperature. The use of a refrigerator allows unattended operation for indefinite periods of time. The cell has been used to obtain spectra between 95 and 220 Kelvin with our diode laser spectrometer and with the 1-m FTS at Kitt Peak.
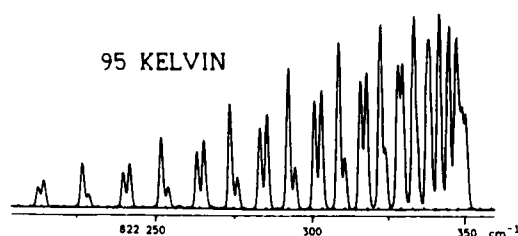
(A) The $^{R}Q_0$ region in the 12-micron band of ethane, recorded with a sample temperature of 95 Kelvin. The linewidth is 0.0017 cm^{-1} FWHM.
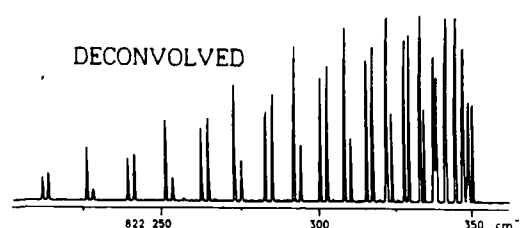
(B) The same spectrum as (A) deconvolved to remove the doppler lineshape. The resulting linewidth is 0.0006 cm^{-1} FWHM.

Adress of authors: Planetary Systems Branch, Code 693.2, NASA Goddard Space Flight Center, Greenbelt, MD 20771.

TB2.   (8:42)

TEMPERATURE DEPENDENCE OF THE H_2-BROADENING COEFFICIENT FOR THE ν_9 FUNDAMENTAL OF ETHANE

J. J. HILLMAN, G. W. HALSEY, AND D. E. JENNINGS

Recently the vertical distribution of Jovian ethane was determined from ultra-high resolution, infrared heterodyne measurements of individual stratospheric lines near 12 microns[1]. Due to uncertainties in the temperature dependence of some of the molecular parameters, we undertook an investigation of the spectrum of ethane under H_2-broadened conditions. These spectra were recorded at Doppler-limited resolving power with the GSFC tuneable diode laser spectrometer. Using our new low-temperature absorption cell we have studied the temperature dependence of this line broadening over the range 95-220K. We will discuss this experiment, the basic results, and the implications for the retrieved Jovian vertical ethane distribution.

1   T. Kostiuk, et al., Ap. J. 265, 564 (1983) see also T. Kostiuk, et al.,
    BAAS, 17, 703 (1985).

Address of Authors: Laboratory for Extraterrestrial Physics, NASA/Goddard
Space Flight Center, Greenbelt, Maryland 20771

TB3. (8:54)

DETERMINATION OF THE $^{16}O^{12}C^{32}S$ ν_3-FUNDAMENTAL BAND STRENGTH FROM DIODE LASER MEASUREMENTS

T. E. BLACKBURN, C. CHACKERIAN JR., M. LOEWENSTEIN, J. R. PODOLSKE

The band strength of the ν_3-fundamental band of $^{16}O^{12}C^{32}S$ at 2062 cm^{-1} has been determined from measurements made with a tunable diode laser spectrometer. For this analysis of the ν_3 band, individual isolated lines throughout the P and R branches and out to $J = 77$ have been measured. Individual line strengths were determined from fits of Voigt profiles to the line data. The requisite care has been exercised to assure that the diode laser source radiation is single-mode.

From the individual line strengths, the band Herman-Wallis factor, and the total band strength have been determined. Comparison with previous measurements of the ν_3-fundamental band strength will be presented.

Address of Authors: NASA/AMES RESEARCH CENTER, MS 245-5, Moffett Field, CA 94035

TB4. (9:06)

MEASUREMENT OF HYDROGEN-BROADENED LINE WIDTHS OF CO AT LOW TEMPERATURES

P. VARANASI, S. CHUDAMANI, AND S. KAPUR

Prompted by the need expressed by astronomers observing the 5 μm spectra of Jupiter and Saturn, we have measured hydrogen-broadened half-widths of several lines in the P- Branch of the fundamental band of ^{12}CO at 100, 150, 200, 250, and 298 K in our laboratory. We have employed a tunable diode laser spectrometer and the sweep-integration technique. The variation of the line widths with temperature may be described according to the empirical power law :

$$\gamma_J^o \sim T^{-n}$$

with n = 0.678 + 0.005 .

Address of the authors: Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, NY 11794-2300

TB5.   (9:23)

AIR-BROADENED HALFWIDTHS IN THE ν_3 BAND OF $^{12}CH_4$

D. CHRIS BENNER, CURTIS P. RINSLAND AND V. MALATHY DEVI

A series of high-resolution (0.01 cm^{-1}) room-temperature spectra of a lean mixture of natural methane in dry air was recorded in the ν_3 region of CH_4 with a signal-to-RMS noise of a few hundred using the Fourier transform spectrometer in the McMath telescope of the National Solar Observatory. Total pressures of up to 500 Torr were employed with an absorption path of 50 cm and a mixing ratio of about 0.0025. A non-linear least squares spectral fitting technique has been applied to determine positions, intensities and air-broadened halfwidths of individually resolved spectral lines. The experimentally determined halfwidths will be compared to previously reported values.

Address of Benner and Malathy Devi: Department of Physics, College of William and Mary, Williamsburg, VA 23185
Address of Rinsland: NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23665

TB6.   (9:35)

ABSOLUTE LINE INTENSITIES OF NO AND PRESSURE BROADENING COEFFICIENTS FOR NO-N$_2$ MIXTURES

T. G. Neiss, R. W. Lovejoy, and C. Chackerian, Jr.

Several R-branch line intensities of the 1←0 infrared band for pure NO have been measured at room temperature using a tunable diode laser spectrometer. The experimental results deviate by 4 percent on average from calculated values for both the $\pi_{1/2}$ and $\pi_{3/2}$ lines.

Pressure broadening coefficients of NO by N$_2$ have been obtained under conditions appropriate to the stratosphere (10-100 Torr, 220-300°K). The temperature dependence of the broadening data will also be discussed.

Address of Neiss and Lovejoy: Department of Chemistry, Lehigh University, Bethlehem, PA 18015.
Address of Chackerian: Astrophysics Experiments Branch, NASA Ames Research Center, Moffett Field, CA 94035.

TB7.   (9:52)

NEW INFRARED FREQUENCY AND INTENSITY MEASUREMENTS ON CHLORINE MONOXIDE (ClO)

J. B. BURKHOLDER, P. D. HAMMER, C. J. HOWARD, A. G. MAKI, G. THOMPSON, AND C. CHACKERIAN

A Fourier transform spectrometer and tunable diode laser have been used to measure the wavenumbers and relative intensities of the entire 1-0 vibrational band of ClO, including both $^2\Pi_{3/2} - {}^2\Pi_{3/2}$ and $^2\Pi_{1/2} - {}^2\Pi_{1/2}$ transitions for both chlorine isotopes. Measurements of the $^2\Pi_{3/2} - {}^2\Pi_{3/2}$ transitions of the 2-0 band of ^{35}ClO have also been made. Improved rovibrational constants will be given along with improved values for the energy levels and infrared transition frequencies. The Herman-Wallis term describing the rotational dependence of the intensity has been determined from relative line intensity measurements made across the band. From this term it has been possible to determine the 1-0 transition moment and integrated band intensity without measuring the ClO concentration.

Address of Burkholder, Hammer, and Howard: NOAA Environmental Research Laboratories, 325 Broadway, Boulder, CO 80303.

Address of Maki and Thompson: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

Address of Chackerian: NASA Ames Research Center, Moffett Field, CA 94035.

64

THE INTENSITY AND SELF-BROADENING OF OVERTONE TRANSITIONS IN HCN

A. M. SMITH, K. K. LEHMANN, AND W. KLEMPERER

The intensity of the (0,0,5)-(0,0,0) transition at 15 552 cm^{-1} in HCN has been measured using a cw dye laser and an optical pathlength of 0.5 km. Also from a photoacoustic spectrum of HCN, the relative intensity of the (0,1,5)-(0,1,0) hot band transition was determined.

In the (0,0,5)-(0,0,0) band, the self-broadening coefficients were measured for both the P and R branches for J between 0 and 19. For the P branch, they range from about 22 to 49 Mhz/torr; for the R branch, they range from about 15 to 45 Mhz/torr. For both branches, the variation of the self-broadening coefficient with J resembles the J thermal population factor vs. J, which suggests that the collisional broadening is dominated by rotational resonances.

Even though the vibrational density of states in the upper state is much larger than the density of rotational states, the line broadening appears to be fully accounted for by rotational relaxation. Our self-broadening coefficients agree quite well with those of Kortum and Verleger[1] for the (0,0,3)-(0,0,0) band at 9,634 cm^{-1} of HCN. They also agree reasonably well with the rotational only linewidth calculations of Rabitz and Gordon.[2] These results show that a high degree of vibrational excitation has little or no effect on the line-broadening.

[1] G. Kortum and H. Verleger, Proc. Phys. Soc. 63, 462 (1949).
[2] H. A. Rabitz and R. G. Gordon, J. Chem. Phys. 53, 1831 (1970).

Address of Smith and Klemperer: Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.
Address of Lehmann: Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

AN INTERPRETATION OF INFRARED INTENSITIES OF POLYATOMIC MOLECULES

WILLIS B. PERSON

An analysis of infrared intensities of fundamental vibrations can be made to obtain the contributions from the motions of each atom to the intensities of each fundamental vibration. This analysis of intensity data is at least as informative as a corresponding PED (potential energy distribution) analysis of the normal modes of vibration. If nothing else, it certainly provides a basis for the critical examination of calculated intensity parameters (atomic polar tensors, APTs), and it offers some physical insight into the understanding of vibrational intensities of polyatomic molecule.

Address of Person: Department of Chemistry, University of Florida, Gainesville, FL 32611.

TB10. (10:59)

CONCENTRATION INDEPENDENT ABSOLUTE INTENSITY DETERMINATIONS:
A NEW METHOD

C. CHACKERIAN, JR.

We discuss some general considerations for obtaining, independently of any
information on molecular concentration, absolute intensity determinations from relative
line intensity measurements made across the vibration-rotation band of a diatomic
molecule. This new method exploits the effect, first elucidated sixty years ago[1], which
vibration-rotation interaction has on relative rovibrational line intensities in a
vibrational band. This approach is important for vibrational fundamental bands of
diatomic molecules since they cannot be studied by the lifetime method which requires the
radiative relaxation lifetime to be much shorter than competing collisional relaxation
processes. Our new method should be particularly significant for diatomic radical species
whose concentrations can be inferred only indirectly.

[1] J.R. Oppenheimer, Proc. Cambridge Phil. Soc. 23, 327 (1926).

Address of Chackerian: NASA Ames Research Center, MS:245-6,
Moffett Field, CA 94035.

TB11. (11:11)

N_2 AND AIR BROADENING IN THE FUNDAMENTAL BANDS OF HF AND HCl

A. S. PINE AND J. P. LOONEY

N_2 and air broadened lineshapes of HF and HCl transitions in the v=1←0 bands have been
measured at T=295 and 202 K with a high-resolution difference-frequency laser spectrometer.
Pressure broadening and shifts and collisional narrowing parameters have been extracted by
least squares fitting of several collisional profiles to the spectra. At low pressures, the
collisional, or Dicke, narrowing effect causes deviations from the Voigt profile having a
Doppler-fixed Gaussian component and yields a measure of the diffusion constants for the
hydrogen halides in the buffer gases. At high J, where the pressure shifts are comparable to
or larger than the broadenings, a slight asymmetry is observed in the lineshapes which is
attributed to statistical correlation between velocity- and state-changing collisions. The
ratio of air-to-N_2 broadening varies systematically with rotational level and is always
somewhat larger than that given by the relative quadrupolar contributions of O_2 and N_2. The
temperature variations in the broadening coefficients are also J dependent, deviating
significantly from $T^{-1/2}$ and exhibiting opposite behavior for HF and HCl.

Address of Pine: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg,
MD 20899.
Address of Looney: Department of Physics, Pennsylvania State University, University Park, PA
16802.

TB12.   (11:28)

EFFECTS OF COLLISIONAL VELOCITY CHANGES ON LINE SHAPES OF HF BROADENED BY FOREIGN GASES

R. M. Herman and J. P. Looney

The Doppler narrowing of HF vibration-rotation lines in the fundamental band at low pressures of N_2 and O_2 has been observed by Pine and Looney.[1] A treatment for this phenomenon, which represents an extension of the theory of Herman and Weber[2] on velocity change broadening in saturation spectroscopy is presented. Here one analyses the velocity changing effect as an impact phenomenon--that is, in terms of individual collisional events--as opposed to involving the entire diffusional histories[3,4] of the optically active molecules. This is correct if, as in HF line broadening, phase and internal-state-change interruptions occur for collisions which cause small relative velocity changes. Then the effects of large velocity changes are completely lost due to ordinary radiative interruption, so that wide-angle collisions (which dominate the diffusional phenomena) simply cannot influence the lineshapes. Properties of the dipole-dipole correlation function are outlined and their influence on the lineshapes discussed. Comparisons with the data of Pine and Looney will be given, where possible.

[1] A. S. Pine and J. P. Looney, this session.

[2] R. M. Herman and E. W. Weber, J. Phys. B: At. Mol. Phys. 16, 1323 (1983).

[3] L. Galatry, Phys. Rev. 122, 1218 (1961).

[4] S. G. Rautian and I. I. Sobel'man, Soviet Phys. Uspekhi 9, 701 (1967).

Address: Department of Physics, The Pennsylvania State University, University Park, PA 16802

TB13.   (11:45)

LINEWIDTHS AND SHIFTS OF THE FUNDAMENTAL VIBRATION-ROTATION BAND OF HF AND HCL BROADENED BY N_2, O_2 AND AIR

J. P. LOONEY and R. M. HERMAN

The linewidths and shifts of the fundamental vibration-rotation band of HF-X and HCL-X systems (X = N_2, O_2, Air) have been calculated at 202° and 296° K, using the Kolb-Griem-Baranger theory. The calculations include isotropic effects to all orders, use of realistic trajectories (as a modification of straight line trajectories) and explicit velocity averaging. It is found that the major contributions to the linewidths and shifts arise from dipole-quadrupole, quadrupole-quadruople, and vibrationally dependent isotropic dispersion forces. Due to the reduction of the dipole-quadrupole and quadrupole-quadrupole contributions with increasing $|m|$, the widths decrease, with a leveling off at high $|m|$ values, where the dispersion forces dominate.

A comparison between the calculated and measured[1] widths and shifts, which shows good overall agreement, will be given.

[1] A. S. Pine and J. P. Looney, this session.

Address: Department of Physics, The Pennsylvania State University, University Park, PA 16802

TC1. (8:30)

LASER-INDUCED PHOSPHORESCENCE SPECTROSCOPY IN SUPERSONIC JETS. THE LOWEST TRIPLET STATES OF
GLYOXAL, METHYLGLYOXAL, AND BIACETYL [1]

L. H. SPANGLER and D. W. PRATT

We report the first structural study of the lowest triplet states of three α-dicarbonyls
(glyoxal, methylglyoxal, and biacetyl) using the technique of laser-induced phosphorescence
(LIP) spectroscopy in supersonic jets. The 0_o^o band is the strongest band in the LIP spectrum
of glyoxal. But the $T_1 \leftarrow S_0$ transitions of methylglyoxal and biacetyl each exhibit strong
progressions in the torsional vibrations of the methyl groups, showing that these molecules
undergo a conformational change on excitation to the lowest triplet state. A Franck-Condon
analysis of the methylglyoxal spectrum, with proper consideration for nuclear spin statistics,
yields a methyl barrier of $V_3 = 115 \pm 5$ cm^{-1} in this state. This value has been confirmed by
a direct measurement of the tunneling splitting of A and E torsional levels. The hindering
potential in the lowest triplet state of methylglyoxal is substantially different from those
in the ground ($V_3 = 269$ cm^{-1}) and first excited singlet ($V_3 = 190$ cm^{-1}) states. Possible
reasons for these differences are discussed.

Address of Spangler: MS-G738, LANL, Los Alamos, NM 87545.
Address of Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

TC2. (8:47)

ROTATIONAL ANALYSIS OF SOME VIBRONIC BANDS IN THE $^3A_u \leftarrow {}^1A_g$ TRANSITION OF GLYOXAL.
SPIN SPLITTINGS IN THE LOWEST TRIPLET STATE OF THE ISOLATED MOLECULE [1]

L. H. SPANGLER, D. W. PRATT, AND F. W. BIRSS

A rotational analysis of three vibronic bands ($0_o^o, 7_o^2$, and 5_o^1) in the laser-induced
phosphorescence spectrum of glyoxal (CHO-CHO) has been performed. From this analysis we
deduce the rotational, spin-rotation, and spin-spin (plus spin-orbit) constants of the lowest
triplet state of the isolated molecule. ^3A_u Glyoxal has been shown to exist in nearly the
same trans-planar (C_{2h}) configuration as the lowest excited singlet state. Both geometries
are very similar to that of the ground state. The dynamic implications of these structural
findings are discussed. We also compare the spin splittings determined in this work with
those previously measured in the condensed phase, using optically detected magnetic resonance
methods.

Address of Spangler: MS-G738, LANL, Los Alamos, NM 87545.
Address of Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.
Address of Birss: Department of Chemistry, University of Alberta, Edmonton, Alberta, CANADA
T6G 2G2

TC3.   (9:04)

THE PHOSPHORESCENCE EXCITATION SPECTRUM OF JET COOLED BENZALDEHYDE [1]

K. W. HOLTZCLAW AND D. W. PRATT

Recent experiments have demonstrated the feasibility of laser-induced phosphorescence experiments via direct pumping of the triplet state in a supersonic jet. We have extended the method in a probe of the ^{3}A" ($n\pi^*$) system of the simplest aromatic carbonyl, benzaldehyde. Spectra at both low (0.6 cm^{-1}) and moderate (0.06 cm^{-1}) resolution have been obtained. Rotational and vibrational analyses of these data are in progress, the results of which will be given. Comparisons with theoretical and solid state work will be made allowing comment on vibronic coupling between the $^3n\pi^*$ state and a near degenerate $^3\pi\pi^*$ state as well as other issues.

Address of Holtzclaw and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

TC4.   (9:21)

PHOTOLUMINESCENCE STUDIES OF LAYERED TRANSITION METAL PHOSPHORUS CHALCOGENIDES

AND THEIR PYRIDINE INTERCALATION COMPOUNDS

D. A. CLEARY, E. LIFSHITZ AND A. H. FRANCIS

Ultra-violet photo-excitation of $Cd_2P_2S_6$ and $Zn_2P_2S_6$ single crystals produces a characteristic photoluminescence between 2.5 and 1.5 eV. $Mn_2P_2S_6$ exhibits only low energy emission due to transitions between localized d-orbital states. These results are consistent with the electronic band structure model for transition metal phosphorus chalcogenides with the general chemical formula $M_2P_2X_6$ (Cd, Zn, Mg, Mn, X=sulfur or selenium), which predicts highly localized states associated with the transition metal d-orbitals and delocalized, band-like states derived from sulfur and phosphorus orbitals.

When pyridine containing a small amount of water is intercalated into $Cd_2P_2S_6$, the excitation and the photoluminescence spectra are changed substantially. The photoluminescence intensity increases approximately tenfold and the position of the excitation edge is shifted to lower energy by 0.5 eV. Intercalation with anhydrous pyridine does not affect either the excitation spectrum or the photoluminescence spectrum of the host lattice.

Address: Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

TC5.

ANGULAR FACTORS IN THE MULTIPHOTON AND MULTIPOLE PHOTOFRAGMENTATION OF MOLECULES

YING-NAN CHIU

Theoretical formulas are derived for the angular distribution of photo-dissociated fragments via higher-order processes. These will be contrasted with those for the lowest-order one-photon and electric-dipole induced dissociation of a diatomic molecule for which the angular distribution is a function of the angle between the transition dipole moment and the principal molecular axis. Angular factors for higher-order dissociation will depend on the symmetry of the initial and final vibronic states of the photo-excitation and on the dissociating state. For 2^n-pole transition and n-photon processes, such factors will involve irreducible tensors up to $2n^{th}$ rank and the corresponding Clebsch-Gordan vector coupling coefficients. They will also incur special vibronic selection rules. The details of these will be discussed.

Address of Chiu: Center of Molecular Dynamics and Energy Transfer, Department of Chemistry, The Catholic University of America, Washington, D.C. 20064.

TC6.

SPECTROSCOPIC INVESTIGATIONS OF SUPERSONICALLY COOLED BENZOIC ACID DIMER

MENG-CHIH SU AND DAVID L. MONTS

Recently, the laser excitation spectrum of benzoic acid dimer $[(C_6H_5COOH)_2]$ cooled in a supersonic expansion has been reported by McVey[1] and by Ito[2]. We have reinvestigated the spectrum of this hydrogen bonded dimer as part of our investigations of hydrogen bonded complexes. Our results will be presented and compared with those of McVey and Ito.

[1] D.E. Poeltl and J.K. McVey, J. Chem. Phys. **78**, 4349 (1983) and Laser Chem. **2**, 189 (1983).
[2] Y. Tomioka, H. Abe, N. Mikami, and M. Ito, J. Phys. Chem. **88**, 2263 (1984).

Address of Su and Monts: Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701.

TC7.

ANOMALIES IN THE RYDBERG SPECTRUM OF 1,3-CYCLOPENTADIENE

A. SABLJIĆ and R. McDIARMID

The lower Rydberg spectrum of 1,3-cyclopentadiene is composed of a very weak band system superimposed on the broad NV_1 band system plus a very complicated set of bands that consists of a progression of doublets separated by 460 cm^{-1}. Neither the higher Rydberg transitions nor the ion spectrum manifest this splitting. The two sets of progressions have been interpreted as either two independent 3p origins or an asymmetric vibronic progression built on one origin. To resolve this conflict, we have remeasured the one and two photon spectra of both cyclopentadiene and cyclopentadiene-d_6 using both linearly and circularly polarized light. In the 3p spectral region, two band systems are one photon active and two band systems are two photon active. Neither of the one photon bands are two photon active. One of the two photon progressions is of the A_1 symmetry species, a species to which none of the 3p-Rydberg transitions belong. In addition, neither the frequency differences between the various apparent origins nor their isotopic ratios correlate with any of the ground state frequency intervals or isotopic ratios of the molecule. We hope, by the time of this meeting, to have satisfactorily interpreted these data.

Address: National Institutes of Health, Bethesda, MD 20892.

Permanent address of Sabljić: The Rudjer Bošković Institute, Zagreb, Yugoslavia.

TC8. (10:47)

THE SPECTROSCOPY OF UNSTABLE THIOCARBONYL COMPOUNDS

R.H. JUDGE AND D.C. MOULE
DEPT. OF CHEMISTRY
BROCK UNIVERSITY, ST. CATHARINES, ONT. CANADA L2S 3A1

A summary of our recent investigation of the conventional VIS-UV absorption and laser excitation spectroscopy of thiocarbonyl compounds is presented.

The technique of flash pyrolysis coupled with long path length absorption spectroscopy has allowed for the detection of the unstable molecules thioformaldehyde (H_2CS), thioacetaldehyde (CH_3CHS), thioacetone (($CH_3)_2CS$), thiopropynal ($HC\equiv C-CHS$), thioacrolein ($CH_2 = CHCHS$) and thioformyl chloride ($CHClS$).

The more interesting features of the spectra of these molecules are presented as well as a discussion of the molecular dynamics as determined from the vibrational analysis.

TC9. (11:04)

SPECTROSCOPY, LIFETIMES, AND QUENCHING OF THE METHOXY RADICAL

NANCY L. GARLAND AND DAVID R. CROSLEY

The laser spectroscopy of methoxy radicals, CH_3O, have been studied in a room temperature, low pressure flow reactor. Excitation spectra and fluorescence spectra of the $\tilde{A}^2A_1 - \tilde{X}^2E$ system, and fluorescence lifetimes and collisional quenching rate constants for $v'=0-3$ have been measured. F atoms, generated by a microwave discharge in a mixture of CF_4 with Ar or He, abstracted H atoms from CH_3OH to produce the radicals. They were excited to the $\tilde{A}$ state with a frequency doubled, pulsed dye laser operated near 300 nm. The excitation spectra of the (0,0), (2,0), and (3,0) bands, obtained with rotational resolution, are quite complex with no evidence of sub-band structure. Fluorescence spectra show a progression with v_3'' (CO stretch) as well as other bands. The radiative lifetime decreases from 1.92 ± 0.06 to 1.49 ± 0.04 µs as v' increases from 0 to 3. Quenching rate constants for the $v'=0$ level with O_2, CO, CO_2, and N_2O collision partners vary from $4 - 14$ $Å^2$.

Address of Authors: Molecular Physics Department, SRI International, Menlo Park, CA 94025

TC10.   (11:21)

THE TWO-PHOTON SPECTRUM OF THE S_1-S_0 TRANSITION IN GLYOXAL

G. A. BICKEL AND K. K. INNES

We report the observation of the S_1-S_0 two-photon spectrum of glyoxal in the region of 21800 - 25400 cm^{-1}. The excitation source is the H_2 Raman shifted output of a Nd:YAG pumped dye laser. The source yielded tunable output from 0.7 - 1.4 μm and enabled both one and two-color two-photon spectra to be observed.

The two-photon spectrum is complementary to the well-known one-photon spectrum. Many of the observed bands belong to the torsional mode, ν_7, revealing vibrational quanta up to 10 in the excited state and 8 in the ground state. Polarization studies confirm previous excited state vibrational assignments and add new information as well.

Department of Chemistry, SUNY-University Center at Binghamton, Binghamton, NY 13901

TC11.   (11:38)

PHOTOELECTRON SPECTROSCOPY OF N_2O^-, CO_2^-, $(N_2O)_2^-$ and $(CO_2)_2^-$

K. H. Bowen, J. V. Coe, J. T. Snodgrass, C. B. Freidhoff, and K. M. McHugh,

We have recorded the negative ion photoelectron (photodetachment) spectra of the gas-phase negative ions N_2O^-, CO_2^-, $(N_2O)_2^-$ and $(CO_2)_2^-$. Nitrous oxide and carbon dioxide are isoelectronic molecules whose negative ions have bent geometries. Due to the large structural differences between these ions and their linear neutrals, appreciable Franck-Condon overlap is not expected during photodetachment transitions between the lowest lying levels of these negative ions and their neutrals. The photoelectron spectra which we obtain for N_2O^- and CO_2^- are consistent with this expectation. Both spectra contain a single broad peak which we interpret primarily as a progression in the bending mode of the neutral. Some structure is visible on this peak in both spectra, it being more pronounced in the CO_2^- spectrum. The maxima of these spectra correspond to electron binding energies of ~1.5 eV for N_2O^- and ~1.4 eV for CO_2^-. These values are interpreted as the vertical detachment energies of N_2O^- and CO_2^-.

In contrast to the similarities between the photoelectron spectra of N_2O^- and CO_2^-, we find substantial differences between the spectra of $(N_2O)_2^-$ and $(CO_2)_2^-$. The photoelectron spectrum of $(N_2O)_2^-$ is similar to that of N_2O^- in that it consists of a single broad peak. Its maximum, however, is shifted by ~0.2 eV to lower electron kinetic energies relative to the maximum in the N_2O^- spectrum, and this represents an increase in the electron binding energy by a corresponding amount. We interpret the $(N_2O)_2^-$ spectrum as arising from the photodetachment of an ionic species which is best described as a bent N_2O^- ion solvated by a neutral linear N_2O molecule, ie. $N_2O^-(N_2O)_1$. The 0.2 eV shift is a rough measure of the ion-solvent dissociation energy of $\overline{N_2O^-(N_2O)_1}$ into N_2O^- and N_2O. By contrast, the maximum in the $(CO_2)_2^-$ photoelectron spectrum has been shifted out of our spectral range. This indicates that the electron binding energy of any maximum in the $(CO_2)_2^-$ spectrum is larger than that for the maximum in the CO_2^- spectrum by at least 1 eV, and that there are substantial differences between $(CO_2)_2^-$ and $(N_2O)_2^-$. While these observations do not definitively distinguish between a simple solvated-ion vs. a more chemical "oxalate-like" bonding picture for $(CO_2)_2^-$, they do suggest that if $(CO_2)_2^-$ is a solvated ion, the interaction energy between CO_2^- and CO_2 is >1 eV.

Address of Investigators: Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218.

TC12.

INTRACONFIGURATIONAL ABSORPTION SPECTROSCOPY OF IrX_6^{2-} IN A_2MX_6 - TYPE HOST CRYSTALS

R.K. YOO and T.A. Keiderling

Results of near-ir absorption spectra for Ir^{+4} in A_2MX_6 (A=K, Rb, NH_4, M=Sn, Pt, X=Cl, Br) type host at 2°K are discussed and compared to earlier work. Our data indicate that the effect of reduced host symmetry is quite small in this d^5 system and that the spectra of $IrCl_6^{2-}$ can be interpreted in a manner paralleling previous studies on Ir^{+4} in cubic hosts. The $IrBr_6^{2-}$ appears to have a somewhat different vibronic pattern. Shifts of zero-phonon origin and the nature of a vibronic progression were analyzed to correlate with host lattice counter-ions. By comparison to luminescence results of Flint and Paulusz, the latter data are proposed to be indicative of a strongly Jahn-Teller active e_g mode.

Address of Yoo and Keiderling: Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, Illinois, 60680, USA.

TE1.

INFRARED ROTATIONAL SPECTRUM OF $\bar{X}$ $^3B_1$ CH_2 AROUND 400 cm^{-1} *

T. J. SEARS

Pure rotational transitions in the methylene radical have been detected at infrared wavelengths. The radical was generated in a discharge in a dilute mixture of ketene (CH_2CO) in helium and the transitions detected at Doppler limited resolution by diode laser absorption. So far, only transitions in the ground vibrational level have been detected, however the signal to noise is such that similar rotational transitions in the (010) level should also be detectable. The rotational levels involved (K_a = 3,4) are much higher in energy than any previously observed and their positions will enable further refinement of the CH_2 X $^3B_1$ potential function. The study also demonstrates the utility of long wavelength infrared laser spectroscopy for detecting rotational spectra of light molecules and transitions between high rotational levels of the CH radical have also been detected with extremely high signal/noise.

Address of Sears: Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973.

TE2.

DIODE LASER SPECTROSCOPY OF THE v_2 BAND OF CH_2

M.D. MARSHALL AND A.R.W. MCKELLAR

The v_2 (bending) fundamental of CH_2 in its ground $^3B_1$ state was first studied[1] using the laser magnetic resonance technique; 10 different rotation-vibration transitions were detected. Later a tunable diode laser was used[2] to observe v_2 in CD_2 and one further transition in CH_2. We have now greatly extended the study of CH_2 by measuring 53 new transitions in the v_2 band in the regions 800 to 911 and 1030 to 1173 cm^{-1}. We use a diode laser spectrometer, Zeeman modulation, and a multiple reflection cell as in the earlier work,[2] but find somewhat different optimum conditions for CH_2 production, namely a mild discharge through a flowing mixture of ketene ($\approx$0.2 torr) and helium ($\approx$2 torr). Discharge modulation was also used to detect the CH_2 absorption, but the sensitivity was worse than for Zeeman modulation, partly because the CH_2 exhibited a surprisingly long lifetime ($\approx$1 ms) following the cutoff of the discharge.

The new transitions extend to higher values of N (10) and K_a (3) than were observed previously. Most important are 10 P- and Q-branch transitions of the K_a = 2 ← 3 sub-band, since neither K_a"=3 nor K_a'=2 had been observed previously. A combined analysis of the available[1,2,3] data results in improved CH_2 parameters, notably for the spin-rotation interaction constant ϵ_{aa}.

[1] T.J. Sears, P.R. Bunker, and A.R.W. McKellar, J. Chem. Phys. 77, 5363 (1982).

[2] A.R.W. McKellar, C. Yamada, and E. Hirota, J. Chem. Phys. 79, 1220 (1983).

[3] T.J. Sears, P.R. Bunker, A.R.W. McKellar, K.M. Evenson, D.A. Jennings, and J.M. Brown, J. Chem. Phys. 77, 5348 (1982).

Address of Marshall and McKellar: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

TE3. · (2:04)

TIME-RESOLVED DIODE LASER SPECTROSCOPY OF THE CCH RADICAL PHOTOCHEMICALLY GENERATED FROM ACETYLENE

H. KANAMORI AND E. HIROTA

We have recently detected the $CCH(X^2\Sigma)$ radical by 193nm ArF excimer laser photolysys of acetylene. Over a hundred absorption peaks are observed in $1750-1900cm^{-1}$ region and time profiles of all the absorption peaks show that the species are produced not instantaneously and decay in 10 micro seconds at the pressure of 100mTorr acetylene. When some buffer gas(H_2 or CH_4) is added, the time profiles change drastically and each peak shows its characteristic behavior, so that the ground state CCH lines are distinguished from many other lines by using this kinetic information. Molecular constants $(B',D',\gamma',$ and $\nu_0)$ of the ν_3 band are detemined by fixing the ground state constants to a previous MW result.[1]

1. K.V.L.Sastry et al., Astrophys.J. 251, L119 (1981)

Address of Kanamori and Hirota: Institute for Molecular Science, Okazaki 444, Japan.

TE4. (2:16)

A NEW ASSIGNMENT OF THE NO_3 1490 cm^{-1} BAND TO AN ELECTRONIC TRANSITION

K. KAWAGUCHI, T. ISHIWATA, I. TANAKA, AND E. HIROTA

In a privious paper,[1] we have reported the observation of the infrared spectrum of NO_3 in the 1490 cm^{-1} region by using a Zeeman modulation diode laser spectrometer. The spectrum was assigned to the ν_3 fundamental($\perp$) band in the $^2A_2'$ state, however some anomalous features have been recognized; (1) the observed Coriolis ccupling constant ($\zeta=0.19$) was much different from the value ($\zeta=0.7$) calculated from a force field, (2) the observed spin-rotation coupling constant($\varepsilon_{cc}=0.11$ cm^{-1}) was much larger than the expected value ($\varepsilon_{cc}<0.06$ cm^{-1}) both for the upper and lower states.

In the present study combination differences have been calculated from the extensively observed transition frequencies to evaluate molecular constants for each state separately and to clarify the effects of perturbations. No evidence for perturbations was found in the lower state (K=0-21) and the spin-splitting could be expressed by only ε_{bb} parameter. The lower state was assigned to the $^2A_2'$ state. On the other hand a spin-orbit interaction constant ($a\xi d=0.17$ cm^{-1}) was indispensable to explain the spin-splitting in the upper state. The ε_{cc} parameters could not be determined in the upper and lower states. A higher-order perturbation was also recognized in the k=7 and k=10 levels of the upper state, however the effect was too small to explain the discrepancy between the observed and calculated ζ constants. The present analysis indicates that the observed upper state is not the ν_3 excited state of the $^2A_2'$ ground state, but an excited electronic state of $^2E''$ or $^2E'$ symmetry.

[1] T. Ishiwata, I. Tanaka, K. Kawaguchi, and E. Hirota, J. Chem. Phys. 82, 2196(1985).
[2] S. Kamata and S. Iwata, Symp. Molecular Structure, Nagoya (1984).

Address of Kawaguchi and Hirota: Institute for Molecular Science, Okazaki 444. Address of Ishiwata and Tanaka: Department of Chemistry, Tokyo Institute of Technology, Ohokayama, Meguro, Tokyo 152, Japan.

TE5.   (2:33)

HIGH RESOLUTION SPECTROSCOPY OF FREE RADICALS USING A FOURIER TRANSFORM SPECTROMETER

P. D. HAMMER, J. B. BURKHOLDER, AND C. J. HOWARD

The importance of molecular free radicals in understanding atmospheric chemistry has motivated the development and application of numerous techniques to detect and quantitatively measure such species, both in the atmosphere and the laboratory. This report will focus on the use of a Fourier transform spectrometer coupled to a fast flow multipass absorption cell to observe vibrational transitions of transient atmospheric species. Laboratory results will be presented for ClO, FO, HO_2, DO_2, SO, CS, and other free radicals.

The feasibility of this technique is determined mainly by two factors: 1) the ability to generate high concentrations of free radicals, and 2) instrumental considerations relating to the fundamental limitations of the apparatus such as detectors and continuum sources. Both of these considerations will be discussed in relation to our results.

Address of authors: Aeronomy Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, CO 80303.

TE6.   (2:50)

THE FOURIER TRANSFORM INFRARED SPECTRUM OF $CHClS$

CATHERINE M. DEELEY

The first spectroscopic study of thioformyl chloride, $CHClS$, was carried-out by Judge and Moule.[1] They photographed the electronic spectrum between the $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$ and $\tilde{a}^3A'' \leftarrow \tilde{X}^1A'$ states in absorption at a dispersion of 1.5 nm/mm. Apart from this work no other spectroscopic data was available on this molecule until now.

$CHClS$ is a short-lived molecule that is generated by the pyrolysis of chloromethyl-methyl-sulphide, $ClCH_2SCH_3$, at about 600°C (1). The experiment was carried-out using a glass body multipass long path cell with a path length of 7 meters, through which the pyrolysis products flowed continuously. A Bomem FTIR spectrometer was used to collect high resolution ro-vibrational spectra of the fundamentals. The results will be discussed.

[1]R.H. Judge and D.C. Moule, J. Mol. Spec. 113, 77-84 (1985).

Address: National Research Council Canada, The Herzberg Institute of Astrophysics, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A 0R6.

TE7.   (3:25)

GAS PHASE AND MATRIX ISOLATION SPECTRA AND FORCE FIELD OF 3H-DIAZIRINE

B. P. WINNEWISSER, A. GAMBI AND H. REISENAUER

Precise band centers are now available for most of the fundamental bands of gas phase 3H-diazirine, H_2CNN, and its isotopomers $H_2{}^{13}CNN$, $H_2C^{15}N^{15}N$, D_2CNN and HDCNN, and centrifugal distortion constants have also been published for all of these species[1]. Matrix isolation spectra in argon have now also been recorded for these same species. The gas phase and matrix data complement each other, and are used together to circumvent weaknesses in the data from each phase alone. The matrix spectra and the valence force field determined from the data will be presented.

[1] M. Winnewisser, A. Gambi and K. Möller, in "The Chemistry of Diazirines" (M. T. H. Liu, ed.), CRC Press, Boca Raton, in press, 1986.

Address of Winnewisser: Physikalisch-Chemisches Institut, Justus Liebig University Giessen, Heinrich-Buff-Ring 58, D-6300 Giessen, West Germany.
Address of Reisenauer: Institut für Organische Chemie, Justus Liebig University Giessen, Heinrich-Buff-Ring 58, D.6300 Giessen, West Germany.
Address of Gambi: Dipartimento di Spettroscopia, Elettrochemica e Chimica Fisica, Facolta di Chimica Industriale, Universita di Venezia, Calle Larga S. Marta 2137, I-30123 Venice

TE8.   (3:37)

HIGH RESOLUTION MEASUREMENTS AND ANALYSIS OF THE ν_2, ν_3, ν_4, ν_5, and $2\nu_9$ BANDS OF NITRIC ACID

A. G. MAKI, W. B. OLSON, A. FAYT, J. S. WELLS, AND A. GOLDMAN

Both tunable diode laser spectra and Fourier transform spectra have been used to analyze the infrared absorption of the ν_2, ν_3, ν_4, ν_5, and $2\nu_9$ bands of nitric acid, covering the major absorption bands between 800 cm^{-1} and 1800 cm^{-1}. Of these bands only ν_2 is totally free of perturbations. From measurements encompassing all quantum numbers up to J=66, K_a=35, and K_c=60, a set of ro-vibrational constants has been determined that reproduces the entire observed spectrum of ν_2 with exceptional accuracy. The ν_3 band is not so well behaved but constants have been determined that give a very good representation of portions of the observed spectrum. The high J values in the P- and R- branches show evidence of a perturbation from levels located above the ν_3 band. The $2\nu_9$ band has been assigned as an A-type band. The Q-, P-, and R-branch transitions have been measured and assigned and the ΔK_a=2 perturbation between ν_5 and $2\nu_9$ has been verified and taken into account in an analysis of both bands. Band constants will be given along with comparisons of calculated and observed spectra.

Address of Maki and Olson: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

Address of Fayt: Molecular Spectroscopy Laboratory, Université de Louvain Chemin du Cyclotron, 2, B-1348 Louvain-La-Neuve, Belgium.

Address of Wells: Time and Frequency Division, National Bureau of Standards, Boulder, CO, 80303.

Address of Goldman: Department of Physics, University of Denver, Denver, CO 80208.

TE9.   (3:54)

THE ABSORPTION SPECTRUM OF HNO_3 AROUND 7.2 μm

O. LADO-BORDOWSKY, A. PERRIN and A. VALENTIN

The nitric acid absorption spectrum has been recorded between 1 270 and 1 370 cm^{-1} with a very high resolution Fourier transform spectrometer (resolution 3×10^{-3} cm^{-1}). The distillated HNO_3 gas was contained at pressures less than 1 torr in a 12 cm length cell coolable over a temperature range 263 - 288 K. During the analysis of the spectrum the ground state levels calculated with the rotational constants of Maki [1] have proved to be very useful.

[1] A.G. Maki and J.S. Wells, J. Mol. Spectrosc. 108, 17 (1984)

Address of Lado-Bordowsky and Perrin : Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, CNRS, Bât. 221, Campus d'Orsay, 91405 Orsay Cedex, France
Address of Valentin : Laboratoire de Spectronomie Moléculaire, CNRS, Tour 13, Université de Paris 6, 4 Place Jussieu, 75230 Paris Cedex 05, France

TE10.   (4:06)

ABSORPTION OF $^{12}CH_3D$ AT 6-10 μm. FREQUENCIES AND INTENSITIES

G. TARRAGO, M. DELAVEAU, M. DANG-NHU, G. GUELACHVILI

The three bands ν_3, ν_5, ν_6 of $^{12}CH_3D$ contributing to the absorption at 6-10 μm were analyzed as a triad, i.e., by accounting for the Coriolis couplings by a diagonalization method. High resolution spectra ($\delta\sigma = 0.005$ cm^{-1}) recorded by the vacuum FT Spectrometer of our laboratory gave us the whole absorption without any interference with the strong water absorption (in the region of ν_5). The 3240 assigned transitions ($J' \leq 18$), of which about one thousand perturbation allowed transitions, were used for a new refinement of the ground state energies ($\sigma = 0.0003$ cm^{-1} for 2641 GS differences), and for a fit of the triad upper state energies ($\sigma = 0.007$ cm^{-1} for the 3240 data).

The line strengths were calculated according to the strict selection rules on J and symmetry species, but without any restriction on ΔK. The effective dipole moment matrix elements required for the transitions within the triad ν_3, ν_5, ν_6 were previously [1] calculated. Values for the dipole moment derivatives $\delta\mu/\delta q_s$ (s= 3,5,6) were deduced from recent values of the band strengths [2,3] S_3 ands S_4 of $^{12}CH_4$, assuming the $\delta\mu/\delta r_i$, in terms of internal coordinates r_i, to be unchanged by H/D substitution. The line strengths calculated using these values are in surprisingly good agreement with the experimental intensity data presently available for ν_6 and ν_3. Nevertheless, some systematic discrepancies at high J require an intensity analysis involving Herman-Wallis-type corrections. Such an analysis is in progress in collaboration with F. Cappellani and R. Restelli (Ispra, Italy).

The energy and intensity parameters obtained have been used to produce a list of about 6000 transitions ($J' \leq 18$) predicted with line strengths $> 4.10^{-25}$ cm.molecule^{-1} (at 300 K) between 874 and 1695 cm^{-1}.

[1] G. TARRAGO, O.N. ULENIKOV and G. POUSSIGUE, J.Physique,45, 1429-1447 (1984)
[2] M. DANG-NHU, A.S. PINE and A.G. ROBIETTE, J. Mol. Spectrosc.,77, 57-68 (1979)
[3] D.E. JENNINGS and A.G. ROBIETTE, J Mol. Spectrosc.,94, 369-379 (1982).

Address : Laboratoire d'Infrarouge (Associé au CNRS), Université de Paris-Sud, Bâtiment 350, 91405 ORSAY CEDEX, France.

TE11.   (4:18)

MEASUREMENT OF INTENSITIES, HYDROGEN- AND NITROGEN- BROADENED LINE WIDTHS OF CH_3D AT LOW TEMPERATURES

SURYANARAYANAN CHUDAMANI AND PRASAD VARANASI

The spectra of Jupiter and Saturn in the 5 um window contain several lines of CH D. Using a tunable diode laser spectrometer, we have measured hydrogen-broadened and nitrogen-broadened half-widths of several lines in the ν_2 - fundamental band at 100, 150, 200, 250, and 298 K. The nitrogen-braodened line widths are relevant to the study of the 8.6 μm lines of this molecule found in the spectrum of Titan's atmsophere. The variation of the line parameters with temperature is discussed.

Address of the authors: Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, NY 11794-2300

TE12.   (4:35)

TUNABLE DIODE LASER MEASUREMENTS OF ABSOLUTE INTENSITIES AND LINEWIDTHS IN THE ν_6 BAND OF $^{12}CH_3D$ NEAR 8.6 μm

K. B. THAKUR, V. MALATHY DEVI, C. P. RINSLAND, AND M. A. H. SMITH

Absolute line intensities were measured at room temperature for 21 transitions in the $\nu_6(E)$ perpendicular band of $^{12}CH_3D$ in the 1090-1140 cm^{-1} region using a tunable diode laser spectrometer. Although the line intensities were determined with high precision ($\approx$ 3%), the square of the vibrational transition dipole moment matrix element derived from each line intensity varied by several percent ($\approx$ 20%) indicating intensity perturbations, possibly caused by Coriolis interactions with the nearby ν_3 parallel-type fundamental. Room temperature air- and nitrogen-broadened halfwidths have also been determined for these lines. The average of the ratios of nitrogen- to air-broadened halfwidths was 1.01 with a standard deviation of 0.01, indicating almost equal broadening efficiencies for nitrogen and air. Room temperature self-broadened halfwidths were determined for two transitions with a mean value of 0.081 ± 0.010 cm^{-1} atm^{-1}.

Address of Thakur: Physics Department, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio, 43210.
Address of Malathy Devi: Physics Department, College of William and Mary, Williamsburg, Virginia, 23185.
Address of Rinsland and Smith: Atmospheric Sciences Division, Mail Stop 401A, NASA Langley Research Center, Hampton, Virginia, 23665-5225.

TE13.   (4:47)

ON THE ROTATIONAL RAMAN SPECTRUM OF CH_2D_2

W.F. MURPHY

The equilibrium polarizability of the methane molecule is isotropic due to symmetry, so that its rotational Raman spectrum is not allowed. However, this selection rule breaks down due to centrifugal distortion, and a weak rotational Raman spectrum of methane has been predicted on this basis.[1]

The effects of such perturbations may be predicted by considering the matrix elements of the contact transformed polarizability, where the transformation is that used in the perturbation treatment of the vibration-rotation Hamiltonian.[2] The derivation of contact transformed polarizability matrix elements for asymmetric top molecules will be presented, and the rotational Raman spectrum of CH_2D_2, predicted on this basis, will be discussed.

---

[1] A. Rosenberg and K.-M. Chen, J. Chem. Phys. 64, 5304 (1976); Ch.V.S. Ramachandra Rao, J. Mol. Spectrosc. 65, 24 (1977).
[2] D. Papousek and M.R. Aliev, "Molecular Vibrational-Rotational Spectra", Elsevier, N.Y., 1982, p. 206.

Address: Division of Chemistry, National Research Council, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6

TF1.   (1:30)

The Rotational Spectrum and Structure of CF_3H-NH_3

D.D. Nelson, Jr., G.T. Fraser, F.J. Lovas, R.D. Suenram and W. Klemperer

The rotational spectrum of CF_3H-NH_3 has been obtained using two spectrometers, a pulsed nozzle Fourier transform spectrometer and a molecular beam electric resonance spectrometer. A symmetric top spectrum is observed that is consistent with free internal rotation of the NH_3 subunit against the CF_3H subunit. Rotational transitions have been measured in both the ground and first excited internal rotor state of the complex. The spectroscopic constants which have been obtained include: $B_0 = 1996.903(2)$ MHz, $D_J = 3.46(12)$ kHz, and $eQq^N = -3.186(6)$ MHz. From the quadrupole coupling constant of the N nucleus, eQq^N, the bending amplitude of the NH_3 subunit is determined to be $22.57(10)^\circ$. The hydrogen bond length is 2.314(5) A and the weak bond stretching force constant is 0.066(2) mdyn/A. The bond length and stretching force constant for CF_3H-NH_3 are similar to those determined for $HCCH-NH_3$ (2.33 A and 0.070 mdyn/A, respectively).

Address of Nelson and Klemperer: Chemistry Department, Harvard University, 12 Oxford St., Cambridge, MA 02138.
Address of Fraser, Lovas and Suenram: Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C. 20234.

TF2.   (1:47)

VAN DER WAALS POTENTIALS FROM THE INFRARED SPECTRA OF RARE GAS-HF COMPLEXES

G. T. FRASER AND A. S. PINE

High-resolution infrared spectra of the Ar-HF, Kr-HF and Xe-HF van der Waals molecules have been recorded in the vicinity of the H-F stretching fundamentals, ν_1, under thermal equilibrium conditions at T=211 K with a tunable difference-frequency laser. Rotational structure has been observed up to or approaching rotational predissociation, permitting us to model the effective radial van der Waals potentials for these complexes. These potentials provide good estimates for the binding energies, D_0, and the van der Waals stretching frequencies, ν_3, in the ground ($\nu_1=0$) and excited ($\nu_1=1$) states of the molecules. For $\nu_1=0$ in Ar-HF, Kr-HF and Xe-HF, we find $D_0=102$, 133 and 181 cm^{-1} and $\nu_3=39.2$, 41.1 and 43.4 cm^{-1} respectively. The ν_3 modes characterized by the model potentials aid in the assignment of the $\nu_1+\nu_3-\nu_3$ hot bands observed in our spectra. The band centers for the ν_1 fundamentals are all down-shifted in frequency from the isolated HF monomer by $\Delta\nu=-9.654$, -17.518 and -29.185 cm^{-1} for the Ar, Kr, and Xe complexes respectively, indicating that the van der Waals bonds are some 10 to 15% stronger in the excited vibrational state. This increased vibrational attraction also results in a contraction of the van der Waals radial coordinate manifest in the larger rotational constants observed for ν_1; $\Delta B/B_0=+0.35$, $+1.00$ and $+1.75\%$ for Ar-, Kr- and Xe-HF. We have also observed the Q branch of the $\nu_1+\nu_2$ stretch-bend combination band in Ar-HF some 70.2 cm^{-1} above the ν_1 fundamental with a large negative $\Delta B/B_0=-2.00\%$ implying a strong anisotropy in the potential.

Address of Fraser and Pine: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

TF3. (2:04)

ESTIMATES OF THE MOLECULAR QUADRUPOLE AND THE PARALLEL POLARIZABILITY OF BORON TRIFLUORIDE

STEWART NOVICK

The molecular quadrupole moment and the parallel polarizability of boron trifluoride have been calculated from previously measured values of the dipole moments of BF_3 containing van der Waals complexes.[1] The values are

$$\Theta_{zz}(BF_3) = 3.37 \times 10^{-26} \text{ esu cm}^3$$
and
$$\alpha_{//}(BF_3) = 4.88 \times 10^{-24} \text{ cm}^3.$$

It is shown, by the success of this calculation, that previously reported statements[1] on the inapplicability of electrostatic calculations to deduce dipole moments of certain BF_3 containing complexes were in error. The results are used to understand the dipole moment of the complex $HCl\ BF_3$.

[1]K.C. Janda, L.S. Bernstein, J.M. Steed, S.E. Novick, W. Klemperer, J. Am. Chem. Soc. 100, 8074 (1978).

Address: Wesleyan University, Middletown, CT   06457

TF4. (2:16)

PRODUCT STATE DISTRIBUTION OF THE PHOTODISSOCIATION OF THE $NeBr_2$ VAN DER WAALS MOLECULE

J. I. CLINE III, D. D. EVARD, AND K. C. JANDA

Van der Waals molecules formed by rare gas atoms bound to halogen molecules are simple molecular systems on which fundamental theories of chemical dynamics may be tested. Vibrational predissociation of $NeBr_2$ occurs in the reaction

$$NeBr_2(X,v'',J'') + h\nu \rightarrow NeBr_2(B,v',J') \tag{1}$$
$$NeBr_2(B,v',J') \rightarrow Ne + Br_2(B,v'-n,J) \tag{2}$$
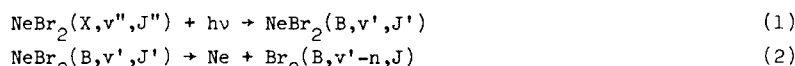
Here X and B indicate the electronic states of $NeBr_2$ corresponding to the associated electronic states of free Br_2 and v is the vibrational quantum number of the Br-Br stretching mode. $NeBr_2(B,v')$ has a lifetime of typically much less than one nanosecond. High resolution laser induced fluorescence studies[1] have yielded accurate structural information about the X and B electronic states of $NeBr_2$ as well as vibrational state dependent rates for (2). The radiative lifetime of $Br_2(B)$ is several orders of magnitude greater than the predissociation lifetime of $NeBr_2$. By dispersing the fluorescence of the Br_2 fragment the vibrational and rotational state distributions of the reaction products are obtained, giving quantum state to state understanding of the reaction dynamics. Further analysis of the spectra allows indirect determination of the depth of the van der Waals potential. Preliminary results show evidence of rotational excitation of the Br_2 fragment and the loss of multiple vibrational quanta upon excitation of the higher v' states.

[1]F. Thommen, D.D. Evard, and K.C. Janda, J. Chem. Phys. 82, 5295, (1985).

Address of Cline, Evard, and Janda: Chemistry Building, University of Pittsburgh, Pittsburgh, PA 15260.

TF5. (2:33)

MOLECULAR BEAM-LASER SPECTROSCOPY OF THE $NeCl_2$ VAN DER WAALS MOLECULE

D. D. EVARD, J. I. CLINE III, F. THOMMEN, AND K. C. JANDA

The $B^3\Pi_{0u}^+ \leftarrow X^1\Sigma_g^+$ systems of Cl_2 and the associated van der Waals molecule $NeCl_2$ formed in a molecular beam have been studied by laser induced fluorescence. Twelve bands originating from $X(v'=0,1)$ have been observed at 0.02 cm^{-1} laser resolution and one band, B-X (9-1) has been examined at 0.001 cm^{-1} laser resolution. The experimental resolution is limited by Doppler broadening and by the homogeneous linewidth of the transition, due to vibrational predissociation, which are on the same order. The excitation spectra were simulated by a model consisting of a T-shaped rigid rotor Hamiltonian for both the ground and excited electronic states. The vibrational predissociation lifetimes, extracted by convolution of the linewidths, range from 29.2 ps for $NeCl_2$ $B(v''=13)$ to 664 ps for $NeCl_2$ $B(v''=7)$. The lifetimes obtained from the lower resolution work agree well with that found in the high resolution spectrum, but the high resolution spectrum is necessary to accurately determine the structural parameters.

Address of Evard, Cline, and Janda: Chemistry Building, University of Pittsburgh, Pittsburgh, PA 15260.

Address of Thommen: CIBA-Geigy, Basel, Switzerland.

TF6. (2:50)

SUB-DOPPLER RESOLUTION INFRARED SPECTROSCOPY OF THE CARBON DIOXIDE DIMER

K.W. JUCKS, Z.S. HUANG AND R.E. MILLER

A computer controlled F-center laser has been used in conjunction with a newly constructed molecular beam apparatus to obtain a completely resolved ro-vibrational spectrum for the carbon dioxide dimer. The dimer vibrational band observed in this study is that associated with the $v_1 + v_2$ band in the monomer at 3714 cm^{-1}.

In order to aid in the assignment of the spectrum, several different source conditions have been used. "Warm" and "Cold" spectra were obtained by expanding 4% and 2% mixtures of CO_2 in He from low and high source pressures, respectively. In order to insure that the spectra did not contain features associated with helium complexes, spectra were also recorded with hydrogen as the carrier gas. These spectra were indistinguishable from those obtained with helium.

As $(CO_2)_2$ is an asymmetric top for which neither the ground or excited state rotational constants are known the assignment of the spectrum is non-trivial and is in progress.

Address: Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27514.

TF7. (3:07)

LASER INDUCED FLUORESCENCE SPECTROSCOPY OF $C_6F_6{}^+ \cdot X_N$ WITH X – He, Ne, Ar, AND N_2

Richard Kennedy, <u>Chung-Yi Kung</u> and Terry A. Miller

The laser-induced fluorescence spectra of ionic clusters $C_6F_6{}^+ \cdot X_N$ are obtained by two-photon ionization of C_6F_6 seeded in a supersonic jet expansion of a mixture of Ne, Ar, or N_2 with He, or pure He. In the case of X=He and Ne, simple progressions in the cluster modes are observed. Quantitative understanding of the $C_6F_6{}^+ \cdot He$ spectrum is possible using a model of the ion-inert gas potential. For $C_6F_6{}^+ \cdot Ar_N$ at relatively low Ar concentration, i.e. -1.0%, a progression of sharp peaks has been observed in contrast to the broader transitions observed at higher Ar concentrations. The red shift of the cluster origin is about 400 cm^{-1}. The spectrum of $C_6F_6{}^+ \cdot (N_2)_N$ shows a similar structure, but with a smaller red shift. The detailed spectral information will be given.

Address of Kennedy: Department of Chemistry, Birmingham University, Birmingham, England.

Address of Kung and Miller: Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

TF8. (3:35)

LASER EXCITATION SPECTRA FOR THE VINOXY-Ar RADICAL
VAN DER WAALS COMPLEX

L.J. VAN DE BURGT, J.C. MALIEKAL and <u>M.C. HEAVEN</u>

Electronic spectra for the vinoxy-argon van der Waals complex (C_2H_3O–Ar) have been recorded for the first time. The complex was formed by photolytically generating vinoxy radicals in the early stages of an Ar free jet expansion. The spectrum was observed by laser excitation of the bands associated with the vinoxy $\tilde{B}\ ^2A''$— $\tilde{X}\ ^2A''$ system. A pair of bands belonging to the complex appeared in conjunction with each of the stronger vibronic bands of the vinoxy excitation spectrum[1] (0_0^1, 1_0^1, 2_0^1, 3_0^1). The complex bands were red shifted from the vinoxy bands by approximately 76 cm^{-1} and 36 cm^{-1}, indicating that electronic excitation strengthens the van der Waals interaction. The influence of the expansion source pressure on the relative band intensities was investigated and found to be consistent with both features arising from a complex which contains a single Ar atom. Thus they are either members of a vibrational progression or bands corresponding to two different structural isomers. In order to distinguish between these possibilities, we are currently analysing rotational contours (recorded at 0.10 cm^{-1} resolution) of the complex bands.

(1). L.J. DiMauro, M.C. Heaven and T.A. Miller, J. Chem. Phys. 81, 2339 (1984).

Address of van de Burgt, Maliekal and Heaven: Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616.

INFRARED PHOTODISSOCIATION OF METHANE-ETHYLENE

S. R. HAIR, AND K. C. JANDA

Photodissociation spectra of CH_4--C_2H_4, CD_2H_2--C_2H_4, and CD_4--C_2H_4 were observed by exciting the ν_7 mode of ethylene in a molecular beam and measuring loss of cluster mass spectrometer signal. Spectra were fit using a two-level lineshape model and homogeneous linewidths were used to determine complex lifetimes. Although momentum gap theory[1] predicts varying lifetimes for the three complexes based on different densities of rotational levels in the cluster fragments, the lifetimes observed are very similar: $\tau(CH_4$--$C_2H_4) \approx 1.8ps$, $\tau(CD_2H_2$--$C_2H_4) \approx 1.8$ ps, and $\tau(CD_4$--$C_2H_4) \approx 1.5$ ps.

[1]G.E. Ewing, Faraday Discuss. Chem. Soc. 73, 325 (1982).

Address of Hair and Janda: Chemistry Building, University of Pittsburgh, Pittsburgh, PA 15260.

ROTATIONAL SPECTRUM, INTERNAL ROTATION, AND STRUCTURE OF Ar-CH_3Cl

G. T. FRASER, R. D. SUENRAM, AND F. J. LOVAS

Rotational spectra of Ar-CH_3Cl, for both Cl isotopes, have been observed using a pulsed nozzle Fourier transform microwave spectrometer. Lower resolution (~ 10MHz) molecular beam electric resonance spectra of these complexes have been previously reported by Steed et al.[1] and DeLeon and Muenter[2]. Steed concluded from the observed spectral complexity that Ar-CH_3Cl is non-symmetrical with a low barrier to internal rotation of the CH_3Cl subunit. DeLeon and Muenter tentatively assigned the spectrum to a rigid rotor. The high resolution spectra that we have obtained allow a definitive assignment of the rotational transitions because of the characteristics Cl nuclear quadrupole hyperfine splittings. The results that we obtain are consistent with the interpretation of Steed. Our assignment for the ground internal rotor state differs from that of DeLeon and Muenter. For the ground internal rotor state the following spectroscopic constants (in MHz) have been obtained:

	Ar-$CH_3{}^{35}Cl$	Ar-$CH_3{}^{37}Cl$
A	13633.047(21)	13436.890(20)
B	1593.584(14)	1565.078(6)
C	1420.448(10)	1395.595(7)
eQq_{aa}	34.89(3)	27.43(3)
eQq_{bb}	-72.18(3)	-56.80(2)

The large shift in frequency of the 1_{01}-1_{10} transition with internal rotor state (ν_A=12040.973(4) MHz and ν_E=14977.107(8) MHz implies nearly free internal rotation of the CH_3Cl subunit. The symmetry axis of the CH_3Cl subunit is nearly perpendicular (~81°) with the line joining the center of mass of the CH_3Cl subunit to the Ar. The center of mass separation is 3.77 A. Centrifugal distortion analysis yields the weak bond stretching force constant and stretching frequency: 0.016(4) mdyn/A and 34(4) cm^{-1} respectively.

[1]J. M. Steed, L. S. Berstein, T. A. Dixon, K. C. Janda, and W. Klemperer, J. Chem. Phys. 71, 4189 (1979).
[2]R. L. DeLeon and J. S. Muenter, J. Chem. Phys., 75, 1113 (1981).

Address of Fraser, Suenram, and Lovas: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

TF11.   (4:21)

METHANOL CLUSTERS OF TRYPTOPHAN ANALOGUES BY PHOTOIONIZATION SPECTROSCOPY

L.A. Peteanu, Y.D. Park, and D.H. Levy

Methanol clusters of two tryptophan analogues, tryptamine and 3-indole pro-
pionic acid have been studied in a supersonic molecular beam using resonantly en-
hanced one and two color photoionization spectroscopy. The two species exhibit
spectral shifts upon complexation which differ both in magnitude and direction.
The effect of the solvent molecule on the qualitative features of the two spectra
is markedly different as well. The spectra of indole propionic acid and trypta-
mine exhibit more than one line in the origin region. These lines have been
assigned to different conformers of each of the two molecules. While the spectrum
of the complexed indole propionic acid is similar to that of the parent species,
in the tryptamine spectrum a single feature predominates. Some implications of
these results for understanding intermolecular interactions within these two clus-
ters will be discussed.

The Department of Chemistry and The James Franck Institute
University of Chicago, Chicago Illinois 60637

TF12.   (4:38)

ROTATIONAL SPECTRA AND STRUCTURE OF DIBORANE-HYDROGEN HALIDE DIMERS*

H. S. GUTOWSKY, T. EMILSSON, J. D. KEEN, T. D. KLOTS, AND C. CHUANG

Rotational spectra of B_2H_6-H/DX complexes are being studied using a Flygare Fourier
transform microwave spectrometer with a pulsed supersonic nozzle as the molecular source. The
most extensive results are for several isotopic species of a B_2H_6-H/DF dimer, observed at 4-18
GHz. The dimer is a near symmetric prolate top (κ = -0.9995); it has a novel, linear BB-H/DF
equilibrium structure with the H/D end of the H/DF attracted axially (a-axis) to a terminal
BH_2 group. The B, C, D_J, and D_{JK} rotational constants for $^{11}B_2H_6$-HF are 2 111.601(1) and
2 091.308(1) MHz, and 5.83(3) and 46.1(5) kHz. The spectra are insensitive to the value of A.

The hyperfine structure of the J = 0 $\rightarrow$ 1 transitions for $^{11}B_2H_6$-HF and $^{10}B^{11}BH_6$-HF shows
that the outer boron nucleus in the dimer has a very small quadrupole coupling ($|\chi_{aa}| \leq 15$
kHz for ^{11}B) while that for the inner boron is appreciable (χ_{aa} of -220 kHz for ^{11}B). The
implications of these results are considered. The hyperfine structure also gives an average
torsional amplitude for the HF and DF of 27° and 25° with respect to the a axis. In-plane
torsional amplitudes of 13.5° were determined for the $^{11}B_2H_6$ and $^{10}B^{11}BH_6$ from the rotational
constants for the HF dimers. With allowance for torsional oscillations, the B...H distance is
2.5032 and 2.5038 Å in the two species. A somewhat smaller B...D distance of 2.4955 Å is
estimated for $^{11}B_2H_6$-DF. The attractive potential between B_2H_6 and HF is estimated from D_J to
have a well depth ε of -530 cm^{-1}, comparable with that reported for N_2-HF.

Rotational transitions have also been identified for the HCl analogue of the "linear"
complex. A study of them is being made to determine from their hyperfine structure whether
the torsional oscillations of the HX are affected by the anisotropy of the terminal BH_2 group.
A search is under way for a non-linear B_2H_6-HF dimer, the possible existence of which is
indicated by observation of three weak unassigned lines requiring both B_2H_6 and HF.

Address: Noyes Chemical Laboratory, University of Illinois, Urbana, IL 61801.

TF13. (4:55)

ROTATIONAL SPECTRA AND STRUCTURE OF THE HCN TRIMER*

R. S. RUOFF, T. EMILSSON, T. D. KLOTS, C. CHUANG, AND H. S. GUTOWSKY

The ground state structure of the HCN trimer has been characterized by Fourier transform microwave observations of its $J = 4 \to 5$ to $J = 7 \to 8$ transitions, using Ar and Ne as carrier gases in a pulsed nozzle system. The trimer is found to be linear. The rotational constants B_o, D_J and a 6th order term H have been determined for five $^{14}N/^{15}N$ isotopically substituted species.

An approximate analysis neglecting torsional oscillations of the subunits, gives their separations r_1 and r_2 to be 3.26 and 3.22 A, respectively, as shown: HCN...$\overset{r}{1}$.HCN...$\overset{r}{2}$.HCN. These values are approximately midway between the intermolecular separation of 3.18 A in the crystalline solid[1] and of 3.28 A in the gas-phase dimer.[2] The ^{14}N quadrupole coupling constants have been determined for each of the three sites in the complex by observations of the mono-HC^{14}N, di-HC^{15}N species.

Further work with HCN is in progress, including a search for the HCN tetramer. The implications of such work will be discussed.

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[1] W. J. Dalmage and W. N. Lipscomb, Acta Cryst. 4, 330 (1951).
[2] L. W. Buxton, E. J. Campbell, and W. H. Flygare, Chem. Phys. 56, 399 (1981).

Address: Noyes Chemical Laboratory, University of Illinois, Urbana, IL 61801.

TF14. (5:12)

Symmetry Classification of the Rotation-Vibration Energy Levels in Ammonia Dimer

D.D. Nelson, Jr., G.T. Fraser, and W. Klemperer

The eigenstates of NH_3 dimer are classified in the molecular symmetry group and the observable microwave spectrum for this system is predicted. Several symmetry groups are examined; each of which admits a different set of permutation-inversion operations. The physical assumptions underlying the choice of each group are detailed and discussed in terms of their acceptability. The microwave spectrum (including hyperfine structure and Stark effects) predicted by each symmetry group is compared with the experimentally observed spectrum.[1] The observed spectrum for the primary isotope consists of two rigid rotor J-J+1, K=0 progressions arising from different vibrational states of the complex. Correlation diagrams are useful to provide physical insight into the nature of these two vibrational states. The microwave spectra of several isotopes of NH_3 dimer have been obtained and the observed isotope effects are readily explained with the assumption of physically reasonable barriers to internal rotation and inversion in the complex. Several recent theoretical calculations[2] of the structure of NH_3 dimer are discussed in the context of these results.

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1) D.D. Nelson, Jr., G.T. Fraser and W. Klemperer, J. Chem. Phys. 83, 6201 (1985).
2) K.P. Sagarik, R. Ahlrichs and S. Brode (to be published).

Address of Nelson and Klemperer: Chemistry Department, Harvard University, 12 Oxford St., Cambridge, MA 02138.

Address of Fraser: Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C. 20234.

TF15. (5:24)

Inversion Effects in the Quadrupole Hyperfine Spectrum of D_2O-CO

K. I. Peterson, D. J. Yaron, and W. Klemperer

Rotational spectra of H_2O-CO, HDO-CO, and D_2O-CO have been obtained with a molecular beam electric resonance spectrometer.[1] The water forms a nearly linear hydrogen bond to the carbon of the CO. The $J=1$, $M_J=1-0$ transition in an external electric field has been obtained at high resolution for all three of these isotopes. There is no evidence of internal motions in the H_2O isomer. The HDO isomer has the deuterium bound to the CO and a quadrupole coupling constant of 230 kHz. The hyperfine spectrum of the D_2O isotope is very close to that expected if the quadrupole coupling constants, eqQ_{aa}, of both deuterons were identical. The spectrum was analysed using a Hamiltonian which allows for incomplete motional averaging of the two eqQ_{aa}'s. The spectra are well fit with an inversion frequency of 1.15 MHz using the geometric expectation for the difference in the eqQ_{aa}'s of 350 kHz.

1) K.I. Peterson, D.J. Yaron, and W. Klemperer, 40th Symposium on Molecular Spectroscopy, Columbus, OH (1985).

Address of Yaron, Peterson, and Klemperer: Chemistry Department, Harvard University, 12 Oxford Street, Cambridge, MA 02138

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TG1.

LASER INDUCED FLUORESCENCE OF THE Rb$_2$ MOLECULE

C. AMIOT and J. VERGES

The laser induced fluorescence of the Rb$_2$ molecule excited from ring dye or Ar$^+$ lasers, has been explored with a high resolution Fourier transform spectrometer.

With styryl 9 dye laser excitation the analysis of the observed fluorescence $A\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$ has given accurate molecular constants for the ground electronic state up to $v = 72$[1].

The 454.5, 457.9, 465.8, 472.7, 476.5 and 488 nm Ar$^+$ laser lines excite the $C\,^1\Pi_u$ state. Visible fluorescence (P , R doublets and Q lines) is observed for the excitation lines. With the last three ones, infrared fluorescence appears in the 4 200 – 5 500 cm^{-1} and 6 200 – 8 000 cm^{-1} spectral ranges. The involved transitions are $C\,^1\Pi_u \rightarrow 1\,^1\Pi_g$ and $C\,^1\Pi_u \rightarrow 2\,^1\Sigma_g^+$. The analysis of these spectra is in progress.

[1] C. Amiot, P. Crozet and J. Vergès, Chem. Phys. Lett. 121, 390 (1985).

Address of Amiot : Laboratoire de Physique Moléculaire et Optique Atmosphérique, CNRS, Bât. 221, Campus d'Orsay, 91405 Orsay Cedex, France.
Address of Vergès : Laboratoire Aimé Cotton, CNRS, Bât. 505, Campus d'Orsay, 91405 Orsay Cedex, France

TG2.

PERTURBATION ANALYSIS IN THE ASUNDI SYSTEM ($a'\,^3\Sigma^+ \rightarrow a\,^3\Pi$) OF $^{13}C^{16}O$ AND IN THE BALLIK-RAMSAY SYSTEM ($b\,^3\Sigma^- \rightarrow a\,^3\Pi$) OF $^{13}C_2$, $^{12}C^{13}C$

C. AMIOT and K. ISLAMI

The molecules were produced by a microwave discharge through $^{13}C^{16}O$ or $^{13}C^{16}O + ^{12}C^{16}O$ mixtures. The spectra were recorded in Laboratoire Aimé Cotton (Orsay) by high resolution Fourier transform spectroscopy.

Very strong perturbations (greater than 10 cm^{-1}) were detected during the rotational analysis of the Asundi system. The vibrational levels $v = 0,1,3$ of the $a'\,^3\Sigma^+$ state interact respectively with the $a\,^3\Pi$ $v = 4,5,6$ levels. The theoretical model we have used include second order spin-orbit and spin-rotation interactions parameters in order to reproduce the observed perturbed wavenumbers to the F.T.S. accuracy (about 0.003 cm^{-1}).

A similar work was performed for the Ballik-Ramsay system interactions. For the three molecules, about 11600 wavenumbers were reduced with a 0.003 cm^{-1} R.M.S. Accurate molecular constants and interaction parameters were derived[1,2]. The variation of the electronic parameters with internuclear distance will be discussed.

[1] C. Amiot and K. Islami, J. Mol. Spectrosc. (to appear)
[2] K. Islami and C. Amiot, J. Mol. Spectrosc. (to appear)

Address of Amiot and Islami : Laboratoire de Physique Moléculaire et Optique Atmosphérique, CNRS, Bât. 221, Campus d'Orsay, 91405 Orsay Cedex, France

TG3. (1:54)

THE OPTICAL SPECTRUM OF NIOBIUM MONOXIDE, NbO

A.G. ADAM, Y. AZUMA, J.A. BARRY, G. CHEVAL, J.L. FEMENIAS, A.J. MERER, and U. SASSENBERG

The optical emission spectrum of NbO consists of a transition near 4700 Å ($C^4\Sigma^--X^4\Sigma^-$) and a complex region of emission from 6000 - 7000 Å. The spectra have been photographed at high resolution using a microwave discharge source, and a rotational analysis of the 4700 Å system performed; there are some most impressive nuclear hyperfine effects in these bands, with line widths of up to 1 cm^{-1}.

For the red region sub-Doppler laser-induced fluorescence spectra of the four sub-bands of the $B^4\Pi-X^4\Sigma^-$(0,0) band near 6700 Å have been recorded. These spectra are incredibly crowded as a result of the hyperfine structure resulting from the I = 9/2 nuclear spin of Nb. The hyperfine structure shows complicated variations with spin state and with J because the ground $^4\Sigma^-$ state has a large second-order spin-orbit splitting of 62 cm^{-1} between its Ω = 1/2 and 3/2 components. The recognition of this large splitting has solved various problems associated with the relationship between the gas spectrum and matrix-isolation data[1].

An unusual intensity cancellation occurs in the hyperfine structure of the low J Q-lines, where certain hyperfine components with $\Delta F = \Delta J$ (which might be expected to be intense) disappear for reasons of geometry.

[1] J.M. Brom, C.H. Durham and W. Weltner, J. Chem. Phys **61**, 970 (1974).

Address of Adam, Azuma, Barry and Merer: Dept of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada V6T 1Y6.
Address of Cheval and Féménias: Laboratoire d'optique atomique et moléculaire, Université de Nice, Parc Valrose, Nice 06034, France.
Address of Sassenberg: Department of Physics, University of Stockholm, Vanadisvägen 9, S-113 46 Stockholm, Sweden.

TG4. (2:11)

LASER SPECTROSCOPY AND STRUCTURE OF MgOH: VIBRATIONAL AND ROTATIONAL ANALYSIS

YONG NI AND DAVID O. HARRIS

Gas phase magnesium hydroxide was produced by the reaction of Mg atoms and H_2O_2 and the A-X system has been studied using a tunable dye laser in the 358-395 nm region. The excitation spectra are complicated. The vibrational analysis and the rotational analysis indicate that MgOH is quasi-linear in both the A and X states. The geometry of MgOH has been determined, and the molecule is well described as a near prolate asymmetric rotor with a Ray asymmetry parameter of less than -0.997.

The results will be discussed and compared to those obtained previously for CaOH, SrOH and BaOH.

Address: Department of Chemistry and Quantum Institute, University of California, Santa Barbara, CA 93106

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LASER SPECTROSCOPY AND STRUCTURE OF MgOH: SPIN-ROTATION INTERACTION

YONG NI AND DAVID O. HARRIS

MgOH is an asymmetric top molecule in the A state. The doublet splittings for N=5-35 in the A state have been observed in the high resolution spectra of MgOH. The splittings fit very well with the formulas given by Henderson and Raynes. The results will be discussed and compared to the spin-rotation interaction of other molecule.

Address: Department of Chemistry and Quantum Institute, University of California, Santa Barbara, CA 93106

LASER-MICROWAVE DOUBLE RESONANCE LASER SPECTROSCOPY OF ALKALINE EARTH MONOHALIDES: HYPERFINE STRUCTURE AND ELECTRIC DIPOLE MOMENTS IN GROUND AND EXCITED STATES

W.E. ERNST

Microwave-optical polarization spectroscopy (MOPS) and molecular beam laser-microwave double resonance techniques have been applied to calcium, strontium and barium monohalides. The precise determination of hyperfine parameters and electric dipole moments provided information about intramolecular fields, field gradients and the charge density distribution which are compared with the results of different bonding models and ab initio calculations.

Address: Department of Chemistry, Stanford University,
         Stanford, California 94305.

OPTICAL-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF SrF:
ANALYSIS OF THE HIGH-LYING $F^2\Sigma^+$ - AND $G^2\Pi$-STATES

J.O. SCHRÖDER, C. NITSCH, AND W.E. ERNST

The $F^2\Sigma^+$ - $B^2\Sigma^+$ and $G^2\Pi$ - $B^2\Sigma^+$ systems of strontium monofluoride were investigated by optical-optical double resonance spectroscopy using two single-mode dye lasers in the rhodamine 6G region. The first laser populated a selected rotational level of the $B^2\Sigma^+$ state, which had been measured previously in our laboratory by Doppler-free polarization spectroscopy[1]. The second laser was scanned and the undispersed UV-fluorescence of the $F^2\Sigma^+$ - $X^2\Sigma^+$ or $G^2\Pi$ - $X^2\Sigma^+$ transition was detected. Energy transfer by collisions gives rise to additional lines. The intensity of these lines decreases rapidly with increasing $|\Delta J|$ of rotational energy transfer.
About 400 lines of the $F^2\Sigma^+$ - $B^2\Sigma^+$(1,0), (2,0), (3,0) band and the $G^2\Pi$ -$B^2\Sigma^+$(0,0) band up to J = 36.5 were measured and assigned. Molecular constants were derived by using a simultaneous fit of the X, B and F or G state including the known $B^2\Sigma^+$ - $X^2\Sigma^+$ line positions for minimizing the correlation between these constants.

[1] W.E. Ernst and J.O.Schröder, Chem.Phys. 78, 363 (1983).

Address: Institut für Molekülphysik, Freie Universität Berlin,
         Arnimallee 14, D-1000 Berlin 33, Germany.

TG8.   (3:42)

THE LAMBDA DOUBLING SPECTRUM OF ^{13}CH, STUDIED BY MICROWAVE-OPTICAL DOUBLE RESONANCE

T.C. Steimle, D.R. Woodward and J.M. Brown

Lambda-doubling transitions in gas phase ^{13}CH in its $X^2\Pi$ electronic state have been observed using the technique of Microwave Optical Double Resonance (MODR). As in previous work[1], the CH radical was generated in situ in a discharge-flow system by the reaction between F atoms and methane. Laser induced fluorescence from the first members of the branches in the (0,0) band of the $A^2\Delta - X^2\Pi$ transitions of ^{13}CH were used in the optical detection.

The frequencies of the hyperfine components of five separate lambda-doubling transitions have been measured and used in to determine the lambda-doubling and hyperfine parameters in the molecular Hamiltonian. The ^{13}C hyperfine parameters will be discussed in terms of the electronic wave function for CH in the $X^2\Pi$ state.

---

[1] C.R. Brazier and J.M. Brown, Can. J. Phys. 62, 1563 (1984).

Address of Steimle: Department of Chemistry, Arizona State University, Tempe, Arizona, 85287

Address of Woodward and Brown: Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, England, OX1 3QZ

TG9.   (3:54)

LASER-INDUCED FLUORESCENCE OF HCO RADICAL.   BRADLEY M. STONE, MARCUS NOBLE, AND EDWARD K.C. LEE

Laser-induced fluorescence from the $(0,9^0,0)$ level of the $\tilde{A}^2\pi A''$ state of the HCO radical has been detected following pulsed dye laser excitation of the $(0,0^1,0)$ level of the $\tilde{X}\,^2A'$ state at 614.48 nm. Fluoroescence emission from $\tilde{A}\,^2\pi A''$ HCO is extremely weak, due to the predissociation of all levels with $1'>0$. The HCO is generated by the photolysis of a 0.2 to 25 torr sample of acetaldehyde vapor at 300K using the 308 nm output of a XeCl excimer laser. Fluorescence excitation and dispersed emission spectra of the $\tilde{A}\,^2\pi A''-\tilde{X}\,^2A'$ transition were recorded. The 644 nm emission reported by Konig and Lademann[1] is not observed. A determination was made of the vibrational frequency of the C-H stretch, $\nu_1'' = 2432$ cm^{-1} + 20 cm^{-1} for the first time in the gas phase, and it is close to the value of 2483 cm^{-1} determined in an Ar matrix.[2] The fluorescence lifetime of $\tilde{A}\,^2\pi A''$ HCO was measured to be <15 nsec, and is shorter than the 46 nsec lifetime reported by Konig and Lademann.[1] The disappearance kinetics of the HCO radical was observed to be second-order in HCO.

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1) R. Konig and J. Lademann, Chem. Phys. Lett., 94, 152 (1983).
2) D.E. Milligan and M.E. Jacox, J. Chem. Phys., 41, 3032 (1964)

Address of Stone: Department of Chemistry, San Jose State University, San Jose, CA. 95192
Address of Noble: Department of Chemistry, University of Southern California, Los Angeles, CA 90007
Address of Lee: Department of Chemistry, University of California, Irvine, CA 92717

TG10. (4:11)

CHEMILUMINESCENT REACTIONS OF MOLECULAR FLUORINE WITH ORGANOSULFUR COMPOUNDS

R. J. GLINSKI, E. A MISHALANIE, AND J. W. BIRKS

The gas-phase reactions of molecular fluorine with organosulfur compounds yield rich chemiluminescence spectra. We have surveyed the chemiluminescence in the wavelength region 400 - 900 nm and in the pressure range 0.2 - 5.0 Torr from the reactions of F_2 with a series of simple organosulfur compounds. Spectral features belonging to emission from vibrationally excited HF, and electronically excited CH_2S and HCF have been unambiguously identified. In addition, a banded spectrum, that weakly underlies the spectra obtained in the reactions of F_2 with nearly all the organosulfur species, is observed distinctly in the reaction of F_2 with CS_2. This feature has not yet been assigned, but $CS_2(a)$ and FCS(A) are the most probable candidates for the emitter. The general characteristics of these spectra and the chemical conditions under which they are observed will be discussed.

Address of Glinski and Mishalanie: National Center for Atmospheric Research, P. O. Box 3000, Boulder, CO 80307.
Address of Birks: Department of Chemistry and CIRES, University of Colorado, Boulder 80309.

TG11. (4:23)

ELECTRONIC SPECTRA OF THIOFORMALDEHYDE, SELENOFORMALDEHYDE, AND OTHER SMALL MOLECULES BY CHEMILUMINESCENCE

R. J. GLINSKI AND J. W. BIRKS

Phosphorescence from the a^3A_2 state of CH_2S, CD_2S, and CH_2Se has been observed in the reactions of F_2 with CH_3SH, CD_3SH, and $CH_3Se_2CH_3$. Details of the vibronic spectra of these molecules will be discussed. The spectral features observed in the reaction of F_2 with CS_2 will also be examined as they relate to $CS_2(a)$ or FCS(A) being the emitter.

Address of Glinski: National Center for Atmospheric Research, P. O. Box 3000, Boulder, CO 80307.
Address of Birks: Department of Chemistry and CIRES, University of Colorado, Boulder 80309.
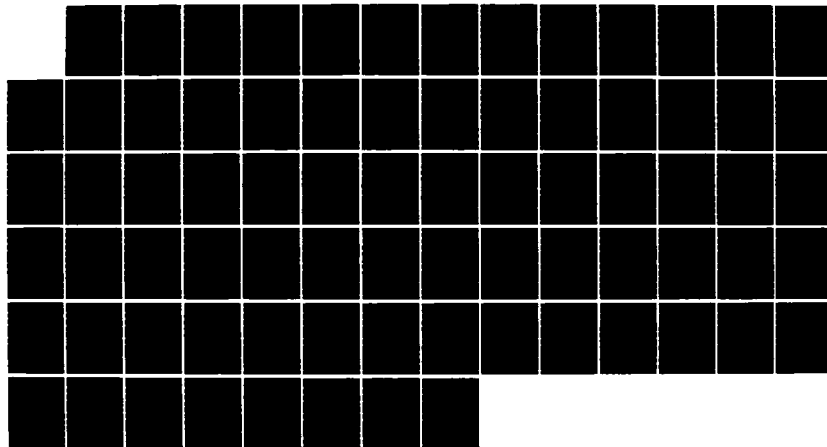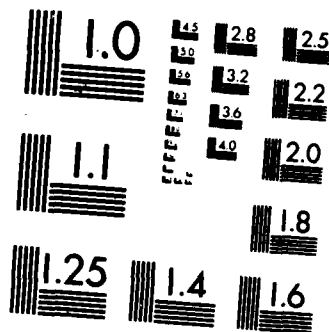
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TG12. (4:40)

QUANTUM BEAT AND ANTICROSSING SPECTROSCOPY OF ACETYLENE WITH 45,000 cm^{-1} OF ENERGY: IMPLICATIONS IN INTERNAL CONVERSION AND INTERSYSTEM CROSSING

P. G. Green, R. W. Field, J. L. Kinsey, E. Abramson, N. Shah, M. Lombardi, P. Dupre, R. Jost

A pulsed, doubled, dye laser is used to excite individual lines in the A ^1A_u-X $^1\Sigma_g^+$ (i.e. S_1-S_0) system. Lines occuring in vibrational bands with 1 to 4 quanta of *trans*-bending vibration have been studied. Quantum beats and anticrossing spectra enable natural lifetime limited resolution in measurements on individual, room temperature, molecules. Anticrossings are seen as dips in the total fluorescence as the applied magnetic field is scanned and nearby triplet levels are tuned into near resonance with the excited singlet. The data reveal interactions of each excited S_1 rovibronic level with nearby triplet levels (T) and extremely highly vibrationally excited levels of the ground electronic state.

Our results shed light on some of the important properties of a molecule with a 'chemically interesting' amount of energy. Densities of vibrational states for the (optically inaccessible) T and S_0 states at this energy can be estimated. The range in size of interaction matrix elements between levels belonging to the (at least) three electronic states involved can be found. These properties determine energy transfer within the molecule by the processes of intersystem crossing (S_1 to T) and internal conversion (S_1 to S_0).

Our 'promoter' model explains clusters of small anticrossings as being a three-way interaction where a large S_1-T anticrossing displaces the S_1 level so that it traverses several nearby S_0 levels, anticrossing with each of them. What we have yet to understand is why anticrossings suddenly display this cluster structure at $v'_3 = 3$ as the number of quanta excited in this *trans*-bending mode is increased. Since SEP experiments (1) have shown that S_0 acetylene displays behavior suggestive of quantum ergodicity at much lower energies, a small increment in energy should not profoundly affect the vibrational character of S_0 levels at 45,000 cm^{-1}; they should each be filling most of the energetically accessible phase space. Moreover, the density of S_0 states is not increasing rapidly: neither the small, fractional increase in their vibrational energy nor dissociation channel effects can produce significant changes here. Thus, S_0 interactions with an S_1-T anticrossing should not change rapidly with energy, yet they seem to do so.

(1) R. L. Sundberg, E. Abramson, J. L. Kinsey, and R. W. Field, J. Chem. Phys. **83**, 466 (1985)

Address of Green, Shah, Abramson, Field, and Kinsey: Department of Chemistry, and G. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.
Address of Lombardi, Jost, and Dupre:
Service National des Champs Intenses, CNRS, 166X CEDEX, 38042 Grenoble, France.

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VIBRATIONAL ANALYSIS OF THE OVERTONE SPECTRA OF CHLOROTRIFLUOROMETHANE

A. M. DE SOUZA AND D. S. PERRY

Vibrational spectra of chlorotrifluoromethane up to the fourth overtone were obtained by photoacoustic spectroscopy and Fourier transform infra-red spectroscopy. The ratio of the single bond anharmonicities to the total coupling between the bonds dictates that this molecule is in the extreme normal mode limit. Twenty one vibrational bands were rotationally simulated to obtain the band origins. The band origins were fitted to the usual normal mode expression to obtain the following spectroscopic constants (in cm^{-1}): $\omega_1^0 = 1111 \cdot 5$; $\omega_4^0 = 1214 \cdot 0$; $x_{11} = -3 \cdot 5$; $x_{14} = -4 \cdot 5$; $x_{44} = -3 \cdot 9$ and $g_{44} = 3 \cdot 7$. A local mode analysis yielded the following parameters (in cm^{-1}): $\omega = 1191 \cdot 2$; $\omega x = -6 \cdot 5$ and $\omega Y = 35 \cdot 8$.

A bond dipole model predicts the relative intensities of vibrations within each manifold are proportional to their local character. The local character of each vibration was approximated in two ways, both giving a qualitative agreement with experimental observations. Molecules in the extreme normal mode limit exhibit a "universal" intensity pattern. A comparison of the above results will be made with other freons molecules.

Address: Department of Chemistry, University of Rochester, Rochester, NY 14627

VIBRATIONAL SPECTRA OF 3-CHLOROCYCLOPROPENE AND ITS DEUTERIUM ISOTOPOMERS; A POTENTIAL FUNCTION FOR THIS MOLECULAR SYSTEM

NORMAN C. CRAIG, JULIANTO PRANATA, JULIAN R. SPRAGUE, SARA JAMIE REINGANUM, AND PHILIP S. STEVENS

Infrared and Raman spectra of 3-chlorocyclopropene and 3-chlorocyclopropene-d_3 were recorded under a variety of sample conditions. From these spectra an essentially complete assignment was made of the vibrational fundamentals of the two molecules. For the d_0 species the frequencies (in cm^{-1}) are: (a') 3171, 3029, 1633, 1266, 1141, 913, 713, 591, 345; (a") 3140, 1034, 1017, 866, 840, 357. An initial set of internal-coordinate force constants was fitted to the frequencies of the d_0 and d_3 isotopomers. Predictions from these calculations guided the assignments of fundamentals in the spectra of a mixture of the two d_1 isotopomers and in the spectra of a mixture of the two d_2 isotopomers. Frequency assignments for all six isotopomers were used to refine a 20-constant potential function -- a general valence function has 66 constants -- to an average frequency fit of about 10 cm^{-1}. In general, interaction constants involving C-Cl motion could not be refined.

Large frequency shifts in CH-rich modes in going from the gas phase to condensed phases correlate with hydrogen bonding effects. This behavior of the 3-chlorocyclopropene molecule may be related to the ease with which this molecule loses the chloride ion to form the cyclopropenyl cation.

Address: Department of Chemistry, Oberlin College, Oberlin, Ohio 44074

WE'3. (2:59)

VIBRATIONAL SPECTRA OF 3-FLUOROCYCLOPROPENE AND 3-FLUOROCYCLOPROPENE-$\underline{d}_3$.

NORMAN C. CRAIG, JULIANTO PRANATA, JULIAN R. SPRAGUE, AND PHILIP S. STEVENS

3-Fluorocyclopropene, a rather labile substance, was prepared from 3-chlorocyclopropene by reaction with AgF$_2$/KF.[1] Infrared and Raman spectra of 3-fluorocyclopropene and its $\underline{d}_3$ isotopomer were recorded. Essentially complete assignments of vibrational fundamentals were made for these molecules. Frequencies for non-CF-rich modes correlate well with those for 3-chlorocyclopropene. In both molecules the two CX bending modes are nearly degenerate. For 3-fluorocyclopropene the fundamental frequencies (in cm^{-1}) are: (a') 3161, 3032, 1623, 1325, 1201, 956, 860(?), 660, 459; (a") 3140, 1060, 1035, 876, 855, 442.

Frequency shifts between the gas-phase and condensed-phase spectra comparable to those caused by hydrogen bonding were found for 3-fluorocyclopropene as for 3-chlorocyclopropene.

Results of normal coordinate calculations for the two isotopomers of 3-fluorocyclopropene will be reported.

[1] N.C. Craig, K.L. Sloan, J.R. Sprague, and P.S. Stevens, J. Org. Chem. 49, 3847(1984).

Address: Department of Chemistry, Oberlin College, Oberlin, Ohio 44074

WE'4. (3:11)

THE VIBRATIONAL SPECTRA AND HARMONIC *AB INITIO* FORCE FIELDS FOR BICYCLO[2.2.1]HEPTANE AND SEVERAL ANALOGS

C. CASTRO, R. DUTLER, A. RAUK, R.A. SHAW, AND H. WIESER

The vibrational spectra in the region of 4000-100 cm^{-1} are reported for 7-oxa- and 7-thia-bicyclo[2.2.1]heptane and bicyclo[2.2.1]hept-2-ene. The spectra of bicyclo[2.2.1]heptane and 2,5-diene are included for comparison. The *ab initio* force fields are calculated at the STO-3G and 3-21G levels for each molecule. The force constants are scaled to fit the observed spectra. The transferability of the scaling factors within this series of compounds is examined for the two basis sets. The optimized force fields are compared with respect to eigenvectors and calculated frequencies.

Address: Department of Chemistry, University of Calgary, Calgary, Alberta, T2N 1N4 Canada.

WE'5. (3:28)

THE VAPOUR PHASE INFRARED SPECTRA IN THE REGION OF 700-100 cm^{-1} OF BICYCLO[3.2.1]OCTANE AND ITS 8-OXA, 6-OXA, 6-OXA-7,7-D$_2$, AND 6,8-DIOXA ANALOGS: EVIDENCE FOR ANHARMONIC SKELETAL DEFORMATIONS

C. CASTRO, N. IBRAHIM, A. RAUK, R.A. SHAW, T.L. SMITHSON, AND H. WIESER

The vapour phase infrared spectra of the title compounds in the region indicated are analyzed explicitly for the purpose of identifying and characterizing the skeletal deformations taking place in the bicyclo[3.2.1]octane ring system. Optimized geometries and harmonic force fields are calculated by *ab initio* methods at the STO-3G level. The force constants are scaled to fit the observed spectra. The skeletal deformations are displayed in terms of the displacement coordinates. One-dimensional anharmonic potential functions are calculated to reproduce observed sequences of Q branches.

Address of Smithson: DREV, 2459 Blvd. Pie XI NORD, C.P. 8800, Courcelette, Quebec, GOA 1R0 Canada.

Address of others: Department of Chemistry, University of Calgary, Calgary, Alberta, T2N 1N4 Canada.

WE'6.   (3:40)

INTERNAL HYDROGEN BONDING IN CYCLIC AMIDES

D. P. McDERMOTT AND V. A. MEIER

This preliminary work will discuss the effects of internal or intramolecular hydrogen bonding on the vibrational dynamics and force fields of cyclic amides. These species are being studied via i.r. and Raman spectroscopy, classical normal mode calculations and MNDO calculations.

The compound of greatest interest is N-(2-hydroxyethyl)-2-pyrrolidinone (HEP), a five-membered cyclic amide. Preliminary i.r. results indicate the presence of internal hydrogen-bonding in HEP, and thus, an additional "ring" which is seven-membered.

Computations focus on the effects of the internal hydrogen bonding upon the normal modes associated with the amide group and subtler effects within the rest of the compound. Preliminary results will be presented and contrasted with other similar work on related cyclic amides.

Address of McDermott and Meier: Department of Chemistry, Lafayette College, Easton, PA 18042, USA.

WE'7.   (3:57)

ON THE NATURE OF HIGH CF_4 VIBRATIONAL LEVELS EXCITED BY PROTON ENERGY LOSS SPECTROSCOPY

HAROLD B. LEVENE and DAVID S. PERRY

The forced harmonic oscillator model, which has been applied to proton energy loss spectroscopy (PELS), is extended here to probe the nature of CF_4 vibrational levels excited by the proton beam. At each overtone of the triply degenerate ν_3 vibration, there is a collection of vibrational sublevels which differ in the way amplitude is distributed among the four C-F bonds. The model predicts that PELS populates a broad distribution of these sublevels with a propensity for the highest energy, most delocalized vibrations in each overtone band. Comparison is made with infrared multiphoton absorption which excites delocalized vibrations in SF_6 and with single photon overtone absorption which selects the most localized states. Peak positions in a simulated spectrum match the experiment up to $8\nu_3$ but for higher overtones the anharmonic shift is up to 0.05 eV less than observed. A demanding test of the model must wait for higher resolution experiments and better spectroscopic constants. It is suggested that high resolution PELS spectra could provide spectroscopic information not accessible by other methods.

Address of Levene: Department of Chemistry, University of California, Irvine, CA 92717
Address of Perry: Department of Chemistry, University of Rochester, Rochester, NY 14627

WF1.

ANALYSIS OF THE Q-BRANCH REGION OF THE $3\nu_3$ OVERTONE OF UF_6: THE IMPLIED STRUCTURE OF THE $n\nu_3$ LADDER. B.J. Krohn, R.S. McDowell, C.W. Patterson, N.G. Nereson, and M.J. Reisfeld

Diode laser spectra of slightly cooled (256 K) UF_6 gas at 3.5 torr were obtained in the 1875 cm^{-1} ($3\nu_3$) region using a 10-m White-type cell built by Kim et al.,[1] in which multiple reflections provided path lengths of 360-400 m. Some of these spectra were reported earlier.[2] Despite the intrinsic weakness of this absorption and the presence of very numerous hot bands at this temperature, we have identified several discrete features as belonging to the transition out of the ground state and have assigned their rotational quantum indices. The wavenumbers were fitted to the vibration-rotation Hamiltonian of Hecht[3] using an interacting-band analysis.[4]

Derived values for $B\zeta_3$ and ΔB are consistent with corresponding values determined from the analysis of the ν_3 fundamental.[5] In addition, we now report Hecht's parameters ω_3^0, X_{33}, G_{33}, and T_{33} for the $n\nu_3$ vibrational overtone ladder of UF_6. The implied ladder structure will be discussed in terms of a "local-type" vs. a "normal-type" interpretation of the ν_3 mode of vibration.

[1] K.C. Kim, E. Griggs, and W.B. Person, Appl. Opt. 17, 2511 (1978).

[2] G.A. Laguna, K.C. Kim, C.W. Patterson, M.J. Reisfeld, and D.M. Seitz, Chem. Phys. Lett. 75, 357 (1980).

[3] K.T. Hecht, J. Mol. Spectrosc. 5, 390 (1960).

[4] C.W. Patterson, B.J. Krohn, and A.S. Pine, J. Mol. Spectrosc. 88, 133 (1981).

[5] J.P. Aldridge et al., J. Chem. Phys. 83, 34 (1985).

Address: University of California, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

WF2.

INFRARED SPECTRA OF TeF_6. ISOTOPE SHIFTS AND FORCE CONSTANTS IN HEXAFLUORIDE MOLECULES

R. S. McDOWELL, R. F. HOLLAND, W. H. McCULLA, G. K. ANDERSON, and M. J. REISFELD

The infrared spectrum of natural TeF_6 and of 99.3% $^{130}TeF_6$ has been recorded using FTIR and grating spectrometers and tunable diode lasers. The isotopic shift in ν_3 (ca. 0.68 cm^{-1}/amu) was measured and rotational structure in the P and R branches was resolved and analyzed. Integrated absorptivities were also measured for the stronger bands. The isotope shifts and Coriolis constants were used to fix the general quadratic symmetry and valence force fields, and the force constants of the Group VI series SF_6, SeF_6, and TeF_6 will be compared and discussed.

A theoretical treatment of the relation between the vibrational frequency ν_3 and central-atom mass m in octahedral XF_6 molecules yields a semi-empirical formula for the isotope shift $\Delta\nu_3$ (in cm^{-1}/amu):

$$\Delta\nu_3 = -4.20 \, \nu_3 \, m^{-1.75},$$

where m is in amu. Frequency shifts obtained from this formula agree with measured shifts for the hexafluorides of S, Se, Mo, Te, W, and U with a mean error of less than 0.02 cm^{-1}/amu. The relative usefulness of $\Delta\nu_3$ and $\Delta\nu_4$ and of the Coriolis constants ζ_3 and ζ_4 in constraining the general quadratic force fields of these molecules will be discussed.

Address: University of California, Los Alamos National Laboratory, Los Alamos, N.M. 87545.

WF3.   (3:04)

FAR-INFRARED SPECTRUM OF METHYLAMINE AND THE GROUP THEORETICAL TREATMENT OF ITS LARGE AMPLITUDE MOTIONS

N. OHASHI, K. TAKAGI, W. J. LAFFERTY, W. B. OLSON and J. T. HOUGEN

We report here the results of a study of the far-infrared spectrum of methylamine obtained on the NBS BOMEM DA3.002 Fourier transform spectrometer. The spectrum was recorded in the wavenumber region 50 to 350 cm^{-1} with an apodized resolution of 0.004 and 0.005 cm^{-1}. The torsional band, as well as pure rotational transitions with higher K_a, fall in this wavenumber region. This molecule has two large amplitude motions, the NH_2-wag and the CH_3-torsion. The spectrum is complicated because of splittings arising from these motions. Assignments were made using polynomial fittings of individual subbands. The $B_1(B_2) \leftarrow B_2(B_1)$ and $E_1 \leftarrow E_1$ transitions were assigned for each subband. Preliminary analysis, carried out using approximate energy level formulae, gives a value for the torsional tunneling parameter in the v=1 excited torsional state which is about 30 times larger than the value for the ground state, in good agreement with the earlier work of Möller and coworkers[1].

We have also carried out a group theoretical treatment for the problem of the large amplitude motions, and have obtained energy level formulae which are expected to be applicable for the global fit of the assigned transitions in the spectrum. This formalism was constructed by applying the concepts of extended permutation-inversion groups.

[1]C. Balorgeot, V. Stern, N. Goff, J. Kachmarsky and K. D. Möller, J. Mol. Spectrosc. **92**, 91-100 (1982).

Address of Ohashi: Department of Physics, Faculty of Science, Kanazawa University, Kanazawa 920, Japan.
Address of Takagi: Department of Physics, Faculty of Science, Toyama University, Toyama 930, Japan.
Address of Lafferty, Olson and Hougen: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

WF4.   (3:21)

THE NONRIGID BENDER HAMILTONIAN MARK TWO

R. BEARDSWORTH, P.R. BUNKER, PER JENSEN, AND W.P. KRAEMER

The Nonrigid Bender Hamiltonian has been developed for calculating the rotation-vibration energy levels of certain triatomic molecules(1). We have modified the Hamiltonian by allowing for the dependence of all perturbation energy denominators on v_2 and K. The computer program (NRBTWO) to diagonalize this Hamiltonian has been written and tested on the H_2O, C_3 and HOC^+ molecules using ab initio and experimentally derived potential functions. The results of these studies, and the comparison with the results obtained from using the original nonrigid bender program (NRBONE) will be discussed. The C_3 molecule is particularly interesting since it is bent in some vibrational states and linear in others; the equilibrium structure is bent.

[1]P. Jensen, Comp. Phys. Reports, 1, 1 (1983).

Address of Beardsworth: Digital Equipment GmbH, 8000 Munich 45, West Germany.
Address of Bunker: Herzberg Institute of Astrophysics, National Research Council, Ottawa, Canada.
Address of Jensen: Department of Chemistry, University of Aarhus, Aarhus, Denmark.
Address of Kraemer: Max-Planck Institute for Astrophysics, Garching, West Germany.

WF5. (3:38)

LOCAL MODE THEORY : ANHARMONIC DEGENERATE OSCILLATORS

F. MICHELOT, J. MORET-BAILLY

The theory of local modes provides a good model for highly excited stretching vibrational states in molecules [1]. Morse oscillators are associated with all equivalent bands : but it is difficult to take into account molecular symmetry so that no general theory is available.

Non degenerate and triply degenerate anharmonic oscillators have been introduced [2] through group chains : these can be generalized to n dimensional anharmonic oscillators with the chain :

$$U(n + 1) \supset U(n) \supset O(n)$$

We propose to associate such an oscillator with each set of n equivalent bonds. As a first approximation $O(n)$ is almost a symmetry group and we may define symmetric coordinates. Next the $O(n)$ symmetry is broken but group algebra allows to build an Hamiltonian in which the dominant operator responsible for the splitting appears and is diagonal.

[1] M. S. CHILD and L. HALONEN, Advances in Chemical Physics Volume LVII
[2] F. IACHELLO and R. D. LEVINE, J. Chem. Phys. _77_, 3046 (1982)

Address of F. Michelot and J. Moret-Bailly : Laboratoire de Spectronomie Moléculaire et Instrumentation Laser, Unité de Recherche associée au CNRS, Université de Bourgogne, 6 Bd Gabriel, 21100 Dijon, France.

WF6. (3:55)

NEW INTERPRETATION OF THE ROTATIONAL QUANTUM NUMBER R FOR TRIPLY DEGENERATE FUNDAMENTALS OF SPHERICAL-TOP MOLECULES

Grigory A. Natanson

It is shown that the accurate rotation-vibrational Hamiltonian evaluated in the finite basis set

$$|J_g 1_\tau R_\tau K_R M\rangle \equiv (-1)^{J-1-K_R} (2R+1)^{\frac{1}{2}} \sum_{K,m} \begin{pmatrix} J & 1 & R \\ K & m & K_R \end{pmatrix} |JKM\rangle |1_\tau m\rangle , \qquad (1a)$$

$$|1_\tau m\rangle \equiv \sum_\alpha {}^{(1)}G_{F_1\alpha}^{m\ *} |F_i \alpha v\rangle , \qquad \tau = g,u \text{ for } i=1,2, \qquad (1b)$$

where the vibrational wave functions $|F_1\alpha v\rangle$ of F_1 symmetry with respect to the feasible permutation (O_h) or permutation-inversion (T_d) group are eigenfunctions of the accurate purely vibrational Hamiltonian, can be represented in the tensor form:

$$H_{eff} = B_v J^2 + 2\sqrt{3}B_v \zeta_v T^{110} + z_{vs}\sqrt{5} T^{220} + z_{vt}(120)^{\frac{1}{2}} T^{224}. \qquad (2)$$

We can thus introduce the "assigned" group SO(3) composed of body-fixed rotations followed by appropriate transformations of the vibrational wave functions $|1_\tau m\rangle$. Note that elements of the group introduced in such a way are not transformations of coordinates and hence cannot be used for deriving selection rules. It can be independently proved that matrix elements of a space-fixed component of the electric dipole moment for transitions from states (1a) to a totally symmetric vibrational state of a Γ_d or O_h molecule (or for the $\nu_6(F_{2u})-\nu_5(F_{2g})$ band of SF_6) behave as if this component were a spherical invariant under action of elements of the "assigned" SO(3) group. For tetrahedral molecules it is also useful to introduce the "assigned" inversion -- the operation which multiplies functions (1a) by the factor (-1). The products of feasible permutation-inversions and the "assigned" inversion generate transformations which belong to the SO(3) group in question and lead to Moret-Bailly's labeling scheme. It is important that levels in clusters have the same assigned symmetry in the ground and first excited states of triply degenerate normal modes.

Address: Department of Chemistry, Northwestern University, Evanston, IL 60201.

WG1.   (2:30)

HIGH RESOLUTION, CW LASER INDUCED CHARGE TRANSFER STUDY OF CO^+ AND N_2^+

C.-H. Kuo, I. Milkman, Y. Al-Ramadin, T.C. Steimle, and J.T. Moseley

Numerous transitions involving members of the branches of the (1,0) and (2,0) $A^2\Pi - X^2\Sigma^+$ band of CO^+ and the (5,0) $A^2\Pi - X^2\Sigma^+$ band of N_2^+ have been observed using the technique of Laser Induced Charge Transfer (LICT). This technique uses indirect mass spectroscopic detection to monitor cw dye laser induced electronic transitions. A near room temperature thermal energy distribution of ions was generated using a selected ion flow tube (SIFT) and the transitions were recorded at Doppler limited resolution (FWHM 1.2GHz).

The band systems that were observed showed no indication of heterogeneous perturbations, and therefore an effective Hamiltonian approach was used in the data reduction. The parameters for the v'=5 level of N_2^+ agreed well with those extrapolated from the equilibrium parameters[1]. Equilibrium parameters for the $A^2\Pi$ state of CO^+ were determined by combining our v=1 and 2 results with the previously determined v=0 CO^+ parameters.[2] A discussion of the technique and results will be presented.

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[1] T. A. Miller, T. Sizuki and E. Hirota, J. Chem. Phys. <u>80</u>, 4671 (1984).

[2] R. D. Brown R. G. Dittman, and D. C. McGilvery, J. Mol. Spectosc. <u>104</u>, 337 (1984).

<u>Address of C.-H. Kuo</u>: Department of Chemistry, University of California, Santa Barbara, California 93106.

<u>Address of I. Milkman, Y. Al-Ramadin and J.T. Moseley</u>: Department of Physics, University of Oregon, Eugene, Oregon, 97403.

<u>Address of T.C. Steimle</u>: Department of Chemistry, Arizona State University, Tempe, Arizona, 85287.

INFRARED SPECTROSCOPY OF THE $A^2\Pi_u$ - $X^2\Sigma_g^+$ ELECTRONIC TRANSITIONS OF C_2^-

B.D.REHFUSS, D.-J.LIU, B.M.DINELLI, M.-F.JAGOD, M.W.CROFTON and T.OKA

Since the discovery of the $B^2\Sigma_u^+$ - $X^2\Sigma_g^+$ electronic transitions of C_2^- in the optical region by Herzberg and Lagerqvist[1], many experimental and theoretical works have been reported for this interesting molecular ion. While both the $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$ states have been well understood, the only information on the $A^2\Pi_u$ state is from the optical photo-detachment cross-section study by Mead[2] et al., in which they obtained the information from the pertubations on the $B^2\Sigma_u^+$ energy levels. We observed the high resolution absorption spectrum of the C_2^- $A^2\Pi_u$ - $X^2\Sigma_g^+$ band as part of our project to study carbo-ions. The spectrum was observed in an ac discharge of C_2H_2 and He using the velocity modulation method. Strong lines were observed with a signal to noise ratio of up to 100. About 50 lines have been measured and assigned. Our preliminary molecular constants of the $A^2\Pi_u$ state, together with the results by Mead et al., are listed below:

	This work	Previous work
ν_{00}	3930.288(42)	4002(180)
B	1.6349(5)	1.622(5)
D	$6.33(87)\times10^{-6}$	-
A	-24.977(84)	-24(1)
δ	$8.6(51)\times10^{-4}$	-

We have also observed the (1,1) hot band with good signal to noise ratio indicating very high vibration temperature of C_2^- in the discharge. The analysis of this band will be presented.

[1]G. Herzberg and A. Lagerqvist. *Can. J. Phys.*, **46**, 2363 (1968)

[2]R.D. Mead, U.Hefter, P.A. Schulz and W.C.Lineberger. *J. Chem. Phys*, **82**, 1723 (1985)

Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637.

Permenent address of Dinelli: Istituto di Spettroscopia Molecolare del C.N.R.,Bologna, Italy.

HIGH RESOLUTION LASER SPECTROSCOPY OF SrOCH$_3$

L. C. ELLINGBOE C. R. BRAZIER and P. F. BERNATH

The $\tilde{A}^2E$-$\tilde{X}^2A_1$ transition of strontium monomethoxide has been rotationally analysed at Doppler-limited resolution. SrOCH$_3$ was found to be a prolate symmetric top. The Coriolis coupling of the electronic orbital angular momentum with the rotation about the top axis causes the formally perpendicular band to appear like a parallel transition with all the sub-bands overlapping. Selective laser excitation with narrow-band selective fluorescence detection was used to extract the individual branches from the dense rotational structure. The spectra obtained and the results of their analysis will be discussed.

Address of Ellingboe Brazier and Bernath: Department of Chemistry, University of Arizona, Tucson AZ 85721

WG4.

The $\tilde{A} \leftarrow \tilde{X}$ Systems of the Alkyl-O and Alkyl-S Radicals

Cristino P. Damo, Stephen C. Foster, Yen-Chu Hsu, Xianming Liu, Chung-Yi Kung and Terry A. Miller

Rotationally cold spectra (<5K) of the $\tilde{A} \leftarrow \tilde{X}$ systems of CH_3O, C_2H_5O, iC_3H_7O and CH_3S have been observed by LIF. These radicals were produced by UV laser photolysis of a suitable precursor seeded in a rare-gas free-jet expansion. The "hot" fragments are rapidly cooled by collisions in the expansion and are subsequently probed with a Nd:YAG-pumped dye-laser system. Details of this experimental technique will be presented and the analysis of the CH_3S data will be discussed.

Address: Department of Chemistry, The Ohio State University, Columbus, OH, 43210

WG5.

LASER SPECTROSCOPY OF ISO-PROPOXY AND ETHOXY FREE RADICALS

Xianming Liu, Cristino Damo, Stephen Foster, Chung-Yi Kung, Yen-Chu Hsu and Terry A. Miller

Alkoxy free radicals play important roles in combustion and atmospheric processes. Production of the iso-propoxy and ethoxy free radicals was accomplished by laser photolysis --respectively, third harmonic YAG and KrF excimer--of the corresponding alkyl nitrites seeded into a free jet expansion of a rare gas carrier. Using the output of a tunable dye laser as a probe, we monitored the total fluorescence from the A--X transitions. In both cases reasonably well resolved rotational structure was observed. Both asymmetric tops, the near-oblate iso-propoxy was found to give parallel C-type spectra, while the near-prolate ethoxy was found to give perpendicular C-type spectra. Details of the spectral analyses will be presented.

Address: Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210

WG6.

PROMINENT, AND RESTRICTED, VIBRATIONAL STATE MIXING IN THE FLUORESCENCE EXCITATION SPECTRUM OF BENZOPHENONE [1]

K. W. HOLTZCLAW AND D. W. PRATT

We report the first successful observation of the fluorescence excitation spectrum of benzophenone in the collision-free environment of a supersonic jet. A comparison of this spectrum with an earlier prediction of Heller, et al. [J. Chem. Phys. 73, 4720 (1980)], together with other experimental and theoretical data, reveals the existence of prominent vibrational state mixing of the totally (A) and nontotally (B) symmetric ring torsional modes in the S_1 state, via a cubic anharmonicity term of the form λAB^2. Successful computer simulations of the spectrum show that fully 64 of the 66 vibrational degrees of freedom of this large molecule do not participate in this mixing process. This suggests that the phase space accessible to benzophenone following optical excitation to its S_1 state is extremely restricted. The implications of these findings for intramolecular vibrational relaxation in the electronically excited states of this and other large molecules will be discussed.

Address of Holtzclaw and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

RA2.

AB INITIO CALCULATIONS OF POTENTIAL ENERGY CURVES AND TRANSITION MOMENTS FOR $^1\Sigma_u^+$ STATES OF N_2

WALTER C. ERMLER, JOSEPH P. CLARK, AND ROBERT S. MULLIKEN

The valence, Rydberg, and ion-pair characteristics of three $^1\Sigma_u^+$ states of N_2 are studied in ab initio calculations that include configuration mixing and incorporate selectively optimized basis sets of Slater-type functions. Potential energy curves, as well as transition dipole moments and second moments of charge as a function of internuclear separation, are reported for several states of $^1\Sigma_g^+$, $^1\Sigma_u^+$, and $^1\Delta_u$ symmetries. Transition dipole moments and potential energy curves are in good agreement with those derived from absorption spectra.[1] Spectroscopic constants are reported. Analysis of the second moment and transition moment functions for the lowest $b'^1\Sigma_u^+$ state shows clearly a transformation from atom pair to ion pair to nearly pure Rydberg character as a function of internuclear separation between the separated atoms and united atom limits.

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[1]D. Stahel, M. Leoni and K. Dressler, J. Chem. Phys. _79_, 2541 (1983).

Address of Ermler and Clark: Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030.

Address of Mulliken: Department of Chemistry, University of Chicago, Chicago, Illinois 60637.

RA3.

Theoretical Study of the Electric Dipole Moment Function of the ClO Molecule.

L.G.M. Pettersson, S.R. Langhoff, and D.P. Chong

The ClO radical is an important intermediate species in the chlorine catalytic cycle for the destruction of stratospheric ozone. Measurement of the ClO concentration profile depends critically on an accurate knowledge of the line strength of the 1-0 vibrational-rotational transition.

We have computed the potential energy function and electric dipole moment function (EDMF) for ClO $X^2\Pi$ using several different techniques to include electron correlation. The EDMF is used to compute Einstein coefficients, vibrational lifetimes and dipole moments in higher vibrational levels. The band strength of the 1-0 fundamental transition is computed to be 12 ± 2 cm^{-2} atm^{-1} in good agreement with three experimental values, but larger than a recent value of 5 cm^{-2} atm^{-1} determined from infrared heterodyne spectroscopy. Remaining questions concerning the position of the maximum of the EDMF may be resolved through experimental measurement of dipole moments of higher vibrational levels.

Address of Pettersson and Langhoff: NASA Ames Research Center, Moffett Field, Ca 94035, USA
Address of Chong: Dept of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T1Y6

RA4. (9:49)

Estimation of Vibrational-Rotational Transition Intensities from the
Vibrational Dependance of the Dipole Moment: OH and ClO

D. J. Yaron, K. I. Peterson, and W. Klemperer

Accurate measurements of the dipole moment of OH in the v=0,1 and 2
state (1) and of ClO in the v=0 and 1 state (2) are available.
Approximation of the electric dipole moment function, M(r), by
polynomials in the internuclear separation allows relations between
the transition moments and the dipole moments to be derived. A
reasonably precise value for the transition moment can be obtained
from the dipole moments if the first and second derivatives of M(r) at
r_e are of opposite sign. This is the case for OH but may not be for
ClO. For either molecule, the transition moments are not well
determined by the present amount of experimental data alone. Ab
initio calculations consistently predict certain features of the
dipole moment function. The inclusion of these invariant features
together with the dipole moment values places bounds on the transition
moments. The interaction between vibration and rotation is an
important effect in OH (3) and is included in the analysis.

1) K.I. Peterson, G.T. Fraser, and W. Klemperer, Can. J. Phys. 62,
   1502 (1984).
2) D.J. Yaron, K.I. Peterson, and W. Klemperer, 40th Symposium on
   Molecular Spectroscopy, Columbus, OH, (1985).
3) F.H. Mies, J. Mol. Spec. 53, 150 (1974).

Address of Yaron, Peterson and Klemperer: Chemistry Department,
Harvard University, 12 Oxford street, Cambridge, MA 02138

RA5. (10:06)

SPIN-ORBIT SPLITTING IN FIRST, SECOND, AND THIRD TRANSITION ROW METALS

R.B. ROSS AND W.C. ERMLER

Spin-orbit splitting energies have been calculated for the ^{2}P states
of K, Ca^+, Ga, Ge^+, Br, and Kr^+ and the ^{2}D states of Sc, Ti^+, Cu, and Zn^+
employing an ab initio spin-orbit operator based on relativistic effective
potentials.[1] Splitting energies have also been calculated for their
respective congeners in the second and third transition rows. Spin-orbit
splitting of partially filled p and d subshells into various J states has
been examined as well as spin-orbit splitting in several transition metal
halides. Extended basis sets comprised of Gaussian type functions are
employed to describe valence electrons. Calculated spin-orbit splitting
energies are found to agree to within about 8% of experiment. This is
contrasted to those due to the use of Hartree-Fock wavefunctions and the
full microscopic spin-orbit Hamiltonian, where errors as large as 34%
result for the third transition row elements.

[1] W.C. Ermler, Y.S. Lee, P.A. Christiansen, and K.S. Pitzer, Chem.
   Phys. Lett. 81 70 (1981).

Address of Ross and Ermler: Department of Chemistry and Chemical
Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030

RA6. (10:40)

ELECTRONIC STRUCTURE OF HEAVY-ATOM MOLECULES

Russell M. Pitzer and Nicholas W. Winter

The currently most effective method of treating the electronic structure of molecules containing heavy atoms is to use effective core potentials and spin-orbit operators derived from relativistic atomic calculations (M. Krauss and W. J. Stevens, Ann. Rev. Phys. Chem., 1984; P. A. Christiansen, W. C. Ermler, and K. S. Pitzer, ibid, 1985), as has been demonstrated on a large number of diatomic molecules.

We have re-expressed the spin-orbit operator in a simpler form,

$$\hat{h}_{SO} = \Sigma_\ell \; \varepsilon_\ell(r) \; \hat{\mathbf{l}} \cdot \hat{\mathbf{s}} \; \Sigma_m |\ell m><\ell m|$$

and have written computer programs both to evaluate integrals of this operator over Gaussian atomic orbitals and to transform them to integrals over molecular obitals for polyatomic molecules.

First-order perturbation theory is inadequate to treat the spin-orbit inter-action for heavy atoms, so both the electron-repulsion and spin-orbit matrix elements are included in the CI (configuration interaction) matrix. The CI wavefunctions are intrinsically complex, but with minimal spatial symmetry the CI matrix can be changed to a completely real form. We have written computer programs to do these calculations using C_{2v}, D_2, or D_{2h} double-group symmetry.

Results will be presented for the $5f \rightarrow 5f$ states of PuF_6, and comparisons will be presented with matrix spectra and other types of calculations.

Address of Pitzer Department of Chemistry, The Ohio State University, Columbus OH 43210

Address of Winter Lawrence Livermore National Laboratory, Mail Stop L487, P.O. Box 5508, Livermore, CA 94550

RA7. (10:57)

PHOTOIONIZATION CROSS SECTIONS FOR CO_2 BY THE COMPLEX BASIS FUNCTION METHOD

Chin-hui Yu and C. William McCurdy

The photoionization cross section can be expressed as a particular matrix element of the resolvent of the molecular electronic Hamiltonian. By using a mixture of real and complex Gaussian basis functions to form a matrix representation of the Hamiltonian it is possible to use this expression to compute molecular photoionization cross sections from the results of a matrix diagonalization. This procedure is based on a variational principle for the resolvent matrix element from which the photoionization cross section is calculated, and can be applied in the presence of coupling between ionization channels. The interference between resonance features and the electron-ion scattering background is naturally incorporated by this method, and it is easily implemented for polyatomic systems.

Results are reported for valence ionization of CO_2 at the static exchange level. Agreement with most other calculations is adequate and is especially good with those which compute the photoionization cross section directly from the electron-ion scattering wave function. The complex-basis-function technique is particularly successful in reproducing resonance features in these cross sections. Vibrational averaging over the bending mode, in which the CO_2 molecule possesses the C_{2v} symmetry, has been studied to further the understanding of the nature of the high energy resonance in the $4\sigma_g$ ionization channel.

Address: Department of Chemistry, The Ohio State University, Columbus, OH 43210

RA8.   (11:14)

USING ENERGY DERIVATIVES TO FIND STATIONARY POINTS ON POTENTIAL ENERGY SURFACES

Donald C. Comeau, Robert J. Zellmer, and Isaiah Shavitt

A simple method for using energy derivatives to find stationary points on molecular potential energy surfaces is described. It is based on a least squares fit of the energy and energy derivative data to a polynomial expressed in a minimal subset of the cartesian coordinates of the atoms. Stationary points of this polynomial surface are used to predict the position of stationary points of the molecular surface. These points are used for additional electronic energy calculations and the procedure is iterated to convergence. For calculating frequencies, the polynomial Hessian is transformed back to cartesian coordinates of the atoms for ease of mass-weighting. This method was used to optimize the SCF geometry of CH_3^+ in C_s symmetry. Significant relaxation of the CH_3 portion was observed, in comparison with previous calculations in which that portion was constrained to C_{3v} geometry. The calculated frequencies are reported.

Address: Department of Chemistry, The Ohio State University, Columbus OH 43210

RA9.   (11:31)

AB INITIO VIBRATIONAL TRANSITION DIPOLE MOMENTS AND BAND INTENSITIES OF FORMALDEHYDE

H.C. HSIEH AND W.C. ERMLER

Transition dipole moments and band intensities of asymmetric-top molecules are derived based on a perturbation theory approach that includes anharmonicity effects[1]. Potential energy and dipole moment expansions together with group theoretical analyses for vibrational selection rules are employed. Calculations are carried out using ab initio SCF and CI potential energy surfaces combined with ab initio dipole moment surfaces for the H and D istopes of formaldehyde. Dipole moment expansion coefficients for the three components of the molecule-fixed coordinates, transition dipole moments of fundamental, first overtone, combination and second overtone transitions, and integrated absorption band intensities within the ratio 1:10000 to that of the highest absorption band are reported. Intensity results in terms of band shapes of conventional molecular infrared spectra are also derived and compared to experimental results.

[1] B.J. Krohn and C.W. Kern, J. Chem. Phys. __69__ 5310 (1978).

Address of Hsieh and Ermler: Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030.

RA10.

CENTRIFUGAL DISTORTIONS IN MOLECULES: AN AB INITIO APPROACH

L. L. LOHR AND J.-M. J. POPA

An ab initio approach to the theoretical description of centrifugal distortions in molecules is presented.[1] The method is based on the calculation of the electronic energy changes and gradients accompanying rotationally induced distortions. A centrifugal distortion pathway in nuclear coordinate space is defined. Results are presented at the HF/6-31G** level for NH_3, CH_4, BF_3, and SF_6, and at the Gullemin-Zener level for H_2^+. Quartic centrifugal distortion parameters are computed for each molecule, with distortion anisotropies presented in the form of tensor coefficients. Centrifugally induced electric dipole moment coefficients are presented for CH_4 and BF_3 together with dipole moment changes for NH_3. Agreement with experiment and with conventional theoretical descriptions is generally quite satisfactory, particularly for the tensor coefficients representing the cubic anisotropy in the distortions of the spherical tops CH_4 and SF_6.

[1] L. L. Lohr and J.-M. J. Popa, J. Chem. Phys., in press.

Address of Lohr and Popa: Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

RB1.

SATURATION STARK SPECTROSCOPY AND GLOBAL ANALYSIS OF THE PRINCIPAL ISOTOPIC
SPECIES OF OCS.

J-G LAHAYE, R. VANDENHAUTE and A. FAYT

Saturation Stark spectra of ^{18}OCS, $O^{13}CS$ and $OC^{34}S$ have been recorded with our intracavity CO_2 laser spectrometer.

The following transitions are reported:
$02^00 \leftarrow 00^00$, $03^10 \leftarrow 01^10$, $12^00 \leftarrow 10^00$, $04^00 \leftarrow 02^00$, $04^20 \leftarrow 02^20$, $13^10 \leftarrow 11^10$, $05^10 \leftarrow 03^10$
and $05^30 \leftarrow 03^30$.

This amount of quite accurate measurements has allowed for the first time to perform a global rovibrational analysis of those three principal isotopic species of carbonyl sulfide separately. For each of them, any available zerofield and Stark data has been used. Any off diagonal terms of the Harniltonian (ℓ-type, anharmonic, Stark and polarizability) are considered simultaneously and energy matrices are diagonalized in a one step procedure. A lot of high order parameters are fixed to their values determined for normal OCS. The important effect of anharmonic resonances on the effective dipole moments has been established.
The eq ilibrium parameters of carbonyl sulfide deduced from our analysis will be discussed.

Address: Molecular Spectroscopy Laboratory, Catholic University of Louvain,
2, Chemin du Cyclotron – B-1348 Louvain-la-Neuve – BELGIUM.

RB2.

THE CARBON DIOXYDE MOLECULE : A TEST CASE FOR THE r_o, r_e AND r_m STRUCTURES

G. GRANER, C. ROSSETTI and D. BAILLY

Accurate experimental ground state rotational constants and reliable predicted vibration-rotation interaction constants are available for CO_2 and its isotopic varieties. Therefore CO_2. has been used as a test case to study the various internuclear distances. We found that the r_o. distances are dependent upon the mass of the central carbon atom and that, for a given carbon isotope, r_o is a linear function of the inverse of the reduced mass. This facts allows to interpolate B_o values for ^{17}O containing molecules.

The r_e distances obtained, even from purely 'theoretical' parameters, still show a small isotopic dependence which will be discussed.

Finally we have applied Watson's method[1] to the symmetric and asymmetric varieties of CO_2 to derive the so-called r_m distances. These r_m distances are found to be very close to the r_e distances, the average difference being only 5×10^{-5} A.

[1] J.K.G. WATSON, J. Mol. Spectrosc., 48, 479-502 (1973)

Address : Laboratoire d'Infrarouge (Associé au C.N.R.S.), Bât. 350, Université de Paris-Sud,
91405 ORSAY, Cédex, France

RB3.   (8:54)

FLUOROFORM : A NEW ANALYSIS OF THE POLYAD AT 8-9 MICRONS

G. GRANER and J.P. CHAMPION

High resolution Fourier spectra of CF_3H in the region of ν_2 (A_1), ν_5(E) and $\nu_3 + \nu_6$ (E) have been analyzed in two stages. In the first one[1], a limited matrix model was used (size of the matrices 15x15) and allowed to fit fairly well about 2000 levels, a few of them reaching $J = 50$. In the present stage, a more rigorous theoretical treatment was applied, using a rovibrational Hamiltonian in which all interaction terms between levels are considered up to third order and no matrix truncation is performed.

This better model enabled us to extend in a significant way the assignments : more than 4500 transitions, corresponding to 3500 different energy levels (J up to 55) are now fitted with a s.d. of 0.0007 cm^{-1}.

[1] G. GRANER and G. GUELACHVILI, J. Mol. Spectrosc. 107, 215-228 (1984).

Address of Graner : Laboratoire d'infrarouge (Associé au C.N.R.S.), Bât. 350, Université de Paris-Sud, 91405 ORSAY, Cédex, France

Address of Champion : Laboratoire de Spectronomie Moléculaire et Instrumentation laser (Associé au C.N.R.S.), Université de Dijon, 6 Boulevard Gabriel, 21100 DIJON, France

RB4.   (9:06)

EXPERIMENTAL VALUES FOR THE ROTATIONAL CONSTANTS OF THE OG AND 1G TORSIONAL COMPONENTS OF THE VIBRATIONAL GROUND STATE OF H_2O_2, AND THE MATRIX ELEMENT COUPLING THEM

W. B. OLSON, R. H. HUNT, A. G. MAKI, J. W. BRAULT, AND L. R. BROWN

J. T. Hougen[1] has shown that hydrogen peroxide may be effectively classified as having C_{2h} symmetry. A symmetry based notation which greatly simplifies the description and treatment of H_2O_2 will be introduced. Using capital letters for overall symmetry, sucessive torsional states in an A vibrational state, including the ground state, are labeled 0G, 0U, 1G, 1U, 2G, etc. In vibrations of symmetry B, the U and G labels are interchanged. Symmetry allowed transitions are U <-> G, and symmetry allowed perturbations are G <-> G and U <-> U.

Rotational constants of the OG and 1G torsional states and the matrix element coupling these states have been determined by least squares fitting of combination differences obtained from submillimeter spectra and Fourier transform spectra of the anti-symmetric O-H stretching band, ν_5, and the associated hot band and sum band involving the 1G torsional state. Several series of forbidden transitions provide precise energy differences between the coupled torsional states. The model used for the fitting was an S-reduction Hamiltonian of two asymmetric rotors coupled by a $\Delta K=2$ interaction. The 1G torsional state is at 254.549_3 cm^{-1}. The corresponding torsional mode in the ν_5 and $\nu_2+\nu_6$ vibrational states is about 11 cm^{-1} higher.

Values will be given for the OU - OG torsional splitting in the ν_1, ν_5, $\nu_2+\nu_6$, $2\nu_2$, and $2\nu_6$ vibrational states.

[1] J. T. Hougen, Can. J. Phys. 62, 1392 (1984).

Address of Olson and Maki: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.
Address of Hunt: Department of Physics, Florida State University, Tallahassee, FL 32306.
Address of Brault: Kitt Peak National Laboratory, 950 North Cherry Avenue, P.O. Box 26732, Tucson, AZ 85726.
Address of Brown: Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109.

110

(9:28)

THE STATE OF THE ANALYSIS OF $\nu_9+\nu_4-\nu_4$ OF ETHANE

W. E. BLASS, G. W. HALSEY, D. E. JENNINGS, D. REUTER, AND J. SUSSKIND

Using our preliminary assignment and analysis of diode laser and Fourier transform spectra of the 12 μm region of ethane, an extended model for $\nu_9+\nu_4-\nu_4$ has been constructed and applied to the analysis. Interactions between the upper levels of $\nu_9+\nu_4$ and those of $3\nu_4$, $4\nu_4$, $5\nu_4$ and $6\nu_4$ are included in the current model. Calculated values for the interaction constants have been determined from a combination of a priori calculation results and analysis of torsional splitting data.

These interaction constants as well as the calculated ν_4 overtone levels are used as fixed parameters in a simultaneous 24 state analysis.

The analysis of 1349 upper state energy levels of the hot band yields a standard deviation of 0.0957 cm^{-1}. This result includes several localized resonances which are probably due to the interaction of $\nu_9+\nu_4$ levels with ν_{12} levels. When these locally perturbed levels are removed, the remaining 1098 levels yield a standard deviation of 0.009 cm^{-1}.

The current state of the analysis will be discussed; the analysis methods will be described.

Address of Blass: Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee, 37996-1200.
Address of Halsey, Jennings, Reuter, and Susskind: Planetary Systems Branch, Code 693.2, NASA, Goddard Space Flight Center, Greenbelt, Maryland, 20771.

(9:45)

FIRST STRATOSPHERIC MEASUREMENTS OF CARBONYL FLUORIDE (COF_2) FROM HIGH RESOLUTION INFRARED SOLAR ABSORPTION SPECTRA OBTAINED BY THE ATMOS EXPERIMENT ABOARD SPACELAB 3

C. P. RINSLAND, R. ZANDER, L. R. BROWN, C. B. FARMER, J. H. PARK, J. M. RUSSELL III, AND R. A. NORTON

More than 3000 infrared solar spectra were recorded on 4/29-5/1/85 at ~0.01 cm^{-1} resolution by the ATMOS (Atmospheric Trace Molecule Spectroscopy) experiment during the Spacelab 3 shuttle mission. About 2000 of these spectra are high sun scans; the remaining spectra were recorded over long atmospheric limb paths during sunrise and sunset. These latter spectra show a wealth of absorption features of numerous minor and trace gases in the Earth's thermosphere, mesosphere, stratosphere, and troposphere. We report here the first stratospheric measurements of COF_2 (carbonyl fluoride), a molecule postulated to be an important intermediate product of the decomposition of chlorofluorocarbons (CFC's) in the upper atmosphere.

Absorption features of COF_2 have been identified at 774.0 cm^{-1} and in the 1925-1965-cm^{-1} region of the ATMOS stratospheric spectra. The lower wavenumber feature is the unresolved narrow Q branch of the C-type ν_6 band. Numerous unresolved manifolds of the intense A-type ν_1 band are observed in the higher wavenumber region. ATMOS spectra showing these COF_2 features will be presented.

Address of Rinsland, Park, Russell: NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225.
Address of Zander: Institute of Astrophysics, University of Liege, Liege-Ougree, Belgium.
Address of Brown, Farmer, and Norton: Jet Propulsion Laboratory, Mail Drop 183-301, 4800 Oak Grove Drive, Pasadena, California, 91109.

RB7. (9:57)

THE HIGH RESOLUTION SPECTRUM AND ROTATIONAL ANALYSIS OF THE ν_6 BAND OF CARBONYL FLUORIDE

K. B. THAKUR, R. R. FRIEDL, C. P. RINSLAND, V. MALATHY DEVI, AND K. NARAHARI RAO

The asymmetric top molecule COF_2 has gained additional interest as the presence of the ν_1 and ν_6 bands of it have been observed recently in ~0.01 cm^{-1} resolution spectra of the stratosphere[1]. To provide spectroscopic parameters needed for the analysis of COF_2 absorption in such atmospheric spectra, 0.005 cm^{-1} resolution laboratory spectra of the ν_6 band have been recorded at room temperature and a full rotational analysis has been performed. The laboratory data were obtained with a Bomen Fourier transform spectrometer at the Jet Propulsion Laboratory. Lines in the ν_1 band of OCS were used for calibration.

Although the strong Q branch at 774 cm^{-1} is only partially resolved in the laboratory data, most of the K structure of various J subgroups in the P and R branches is fully resolved. With the help of ground-state rotational constants obtained from the microwave data of Carpenter[2], around 1300 transitions up to J = 40 have been assigned and fitted to a standard deviation of 0.0006 cm^{-1}. By incorporating quartic and sextic centrifugal distortion coefficients of Watson's reduced Hamiltonian into the analysis, upper state rotational constants A, B, and C have been determined to an accuracy better than 10^{-5} cm^{-1}. The results will be discussed along with the asymmetry splitting of the low K transitions for each J.

This work was supported under USAF Agreement RES D5-674 with the Air Force Geophysics Laboratory.

[1] C. P. Rinsland et al., preceding abstract.
[2] J. H. Carpenter, J. Mol. Spectrosc., 50, 182-201 (1974).

Address of Thakur and Rao: Physics Department, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio, 43210.
Address of Friedl: Jet Propulsion Laboratory, Mail Stop 183-601, 4800 Oak Grove Drive, Pasadena, California, 91109.
Address of Rinsland: NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225.
Address of Malathy Devi: Physics Department, College of William and Mary, Williamsburg, Virginia, 23185.

RB8. (10:09)

THE FAR-INFRARED TORSIONAL SPECTRUM OF METHYL SILANE: FREQUENCY AND INTENSITY ANALYSIS

N.M. MOAZZEN-AHMADI, H. JAGANNATH, AND I. OZIER

Fourier transform spectroscopy has been used to study the weakly allowed torsional spectrum of methyl silane. Between 330-380 cm^{-1}, 347 lines in the (v_6=2←0) band were measured at low pressure with a resolution of 0.015 cm^{-1}. Between 150-360 cm^{-1} significant structure and partially resolved features have been observed at moderate pressure with a resolution of 0.15 cm^{-1}. From the low resolution spectrum, 13 Q branch lines for (v_6=3←1) and (v_6=4←2) bands were assigned. A Hamiltonian which included rotational, torsional, and distortion effects to sixth power in angular momentum was used to carry out a simultaneous fit of the infrared transitions, microwave frequencies, and molecular beam splittings. From the best fit, 20 effective rotation, torsion, and distortion parameters were obtained.

The torsional dependence of the electric dipole moment originates from the vibration-torsion-rotation interactions with the nearby excited vibrational states. To degree two in angular momentum this dependence is characterized by 4 parameters. The two "even" moments μ_0^T and μ_2^T are determined from the difference in the Stark shift of the microwave transitions (J=1←0) in the v_6=0 and 2 torsional states. The two "odd" dipole moments μ_1^T and (μ_1^T-μ_1^T) were determined from the lineshape analysis of (v_6=1←0) band of the low resolution data. We show that for methyl silane the centrifugal distortion dipole moments μ_J^Q and μ_K measured from the beam spectrum by Ozier and Meerts should be reinterpreted as linear combinations of the centrifugal and torsional dipole moments. If μ_J^Q and μ_K are fixed at zero, it then becomes possible to calculate μ_1^T and μ_1^T-μ_1^T from the beam data. The results obtained are in agreement with the values determined from the lineshape analysis. We therefore conclude that the torsion distortion effects make a much larger contribution than centrifugal distortion to the variation with the state of the dipole moment in CH_3-SiH_3.

This work was carried out at: Department of Physics, University of British Columbia, 6224 Agriculture Road, Vancouver, B.C., V6T 2A6, Canada.
Present Address of Jagannath: Department of Physics, Alabama A & M University, Normal, Alabama, 35762.

RB9.

LASER-STARK AND FOURIER TRANSFORM SPECTRA OF THE ν_3 BAND OF FORMIC ACID

W.H. Weber, P.D. Maker, and J.W.C. Johns

The 5.6-μm band of HCOOH, which is the strong carbonyl stretch mode, is analyzed using a combination of sub-Doppler resolution laser-Stark data obtained with a CO laser and Fourier transform data obtained from a Bomem interferometer. The Fourier transform data, including 847 lines with J'≤22 and Ka≤11, are fit with a Watson type Hamiltonian to determine excited state constants. The Coriolis interactions with ν_{5+9} and ν_{8+9}, previously noted by Kuze et al.[1], are included in the analysis; the former by using an exact diagonalization technique, the latter via perturbation theory. Taking the molecular parameters from this fit, the laser-Stark data are then analyzed to give ground and excited state dipole moments, yielding the following results in Debye:

$$\mu_a{}'' = 1.4071(8)$$
$$\mu_b{}'' = 0.227(10)$$
$$\mu_a{}' = 1.4353(9)$$
$$\mu_b{}' = 0.214(9),$$

where the errors are 3σ estimates. The laser-Stark data are limited to J'≤7 and give a ±14 MHz fit to 191 lines.

[1] H. Kuze, T. Amano, and T. Shimizu, J. Chem. Phys. 77, 714 (1982).

Address of Weber and Maker: Physics Department, Research Staff, Ford Motor Company, Dearborn, MI 48121.
Address of Johns: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Canada K1A OR6

RB10.

ANALYSIS OF THE COLLISION INDUCED FAR IR SPECTRUM OF CYCLOPROPANE

W. R. GRONLUND, R. C. COHEN, AND W. C. PRINGLE

The far infrared collision induced absorption (CIA) of gas phase cyclopropane (CP) and cyclopropane-rare gas mixtures has been observed. The absorption coefficient for the CP-CP CIA is γmax (70 cm^{-1}) = 7.3 x 10^{-5} (cm^{-1} amagat^{-2}) using $I(\tilde{\nu})/I_o(\tilde{\nu}) = \exp(-\gamma(\tilde{\nu})lP^2)$ where l is the cell length and P^2 is the pressure square.

The theoretical band calculated from the superposition of translationally broadened rotation lines using the literature value of the isotropic polarizability and quadrupole moment of CP with Lennard-Jones pairwise distribution function and a normalized line shape function peaks at 60 cm^{-1} with an absorption coefficient several times smaller that the observed value. This is contrasted with the observed CIA results of other nonpolar hydrocarbons (i.e., allene, ethane, ethylene) which exhibited maxima in CIA bands at frequencies much higher than that calculated from this quadrupole-polarizability term. The frequency distribution of the band for cyclopropane is similar to the results of the more isotropic molecules such as N_2 and CH_4. Intensity variation will be discussed.

Address of Gronlund: Chemistry Section (ds-1), Department of Science, U. S. Coast Guard Academy, New London, CT 06320.
Address of Cohen: Department of Chemistry, University of California-Berkeley, Berkeley, CA 94720.
Address of Pringle: Department of Chemistry, Hall-Atwater Labs, Wesleyan University, Middletown, CT 06457

RB11.

INFRARED-INFRARED DOUBLE RESONANCE IN CH_3F AND NH_3,[1]

SANG K. LEE AND R. H. SCHWENDEMAN

Infrared-infrared double resonance effects have been recorded in CH_3F and NH_3 by using an infrared laser as the pump and an infrared microwave sideband laser system as the signal radiation. The effects of burned holes and transferred spikes in the velocity distributions are clearly seen in 3-level systems. It has been found, however, that pumping a single fundamental transition – the R(4,3) transition in the ν_3 band of $^{13}CH_3F$ or the saQ(8,7) transition in the ν_2 band of $^{14}NH_3$ – increases the intensity of hot band transitions – $v_3 = 2 \leftarrow v_3 = 1$ in $^{13}CH_3F$ or the $v_2 = 2,a \leftarrow v_2 = 1,s$ in $^{14}NH_3$ – even when J and K are very different from the values for the pump. Comparison of the effect of pumping on the intensity of the P(27,15) transition in the ν_3 band of $^{13}CH_3F$ with the effect on the nearby P(20,6) transition in the $2\nu_3 \leftarrow \nu_3$ band shows that the pumping effect is not a simple heating of the sample. Combination of this result with observation of the effect of pumping the R(4,3) transition in the ν_3 band of $^{13}CH_3F$ on the intensity of the Q(12,9) transition in the $2\nu_3 \leftarrow \nu_3$ band of $^{12}CH_3F$ provides qualitative verification of the significant V-V transfer of energy reported previously for these molecules.[2]

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[2]J. M. Preses and G. W. Flynn, J. Chem. Phys. **66**, 3112 (1977).

Address of Lee and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824

RB12.

INFRARED RADIO DOUBLE RESONANCE SPECTROSCOPY OF CF_3Br[1]

WAFAA FAWZY AND R. H. SCHWENDEMAN

Pure nuclear quadrupole resonances in the ground, ν_1, ν_6, and $\nu_1 + \nu_6$ vibrational states of $CF_3^{79}Br$ and in the ground and ν_1 vibrational states of $CF_3^{81}Br$ have been observed in the 1–300 MHz region by applying the infrared radio frequency double resonance (IR-RF DR) technique with a stripline radio frequency sample cell outside the cavity of a semi-sealed CO_2 laser. The 9R(28) and 9R(30) $^{12}C^{16}O_2$ laser lines near 1085 cm^{-1} were used for pumping. In addition to the quadrupole hyperfine structure, A_1-A_2 splittings in the ν_6 and $\nu_1 + \nu_6$ vibrational states of $CF_3^{79}Br$ have been observed. The center frequencies of the observed double resonance effects were determined by fitting the spectra to sums of Lorentzian lineshape functions. Quadrupole coupling constants, determined by least squares fits of experimental frequencies to frequencies calculated by direct diagonalization of the energy matrices, have been obtained for the ground, ν_1, ν_6, and $\nu_1 + \nu_6$ vibrational states of $CF_3^{79}Br$ and for the ground and ν_1 vibrational states of $CF_3^{81}Br$. The ℓ-doubling constants have been determined for the ν_6 and $\nu_1 + \nu_6$ vibrational states of $CF_3^{79}Br$. From the laser coincidences with the assigned transitions, the centers of ν_1 and $\nu_1 + \nu_6 \leftarrow \nu_6$ vibration-rotation bands of $CF_3^{79}Br$ have been estimated. The results of the present work will be compared with previous results obtained by other spectroscopic techniques.

Address of Fawzy and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824.

RB13.   (11:43)

LINESHAPES OF INFRARED RADIOFREQUENCY DOUBLE RESONANCE SPECTRA IN CH_3I[1]

WAFAA FAWZY AND R. H. SCHWENDEMAN

The lineshapes of the F, J, K = 23/2, 9, 8 ← 21/5, 9, 8 "pure" nuclear
quadrupole transition near 360.7 MHz in the ground vibrational state and the
25/2, 10, 9 ← 23/2, 10, 9 transition near 382.9 MHz in the v_6 = 1 state of CH_3,
have been recorded by infrared radiofrequency double resonance (IR-RF DR)
spectroscopy as a function of pressure and radiofrequency power. The infrared
radiation was a $^{12}C^{16}O_2$ laser operating on the 10R(8) transition and the sample
cell was outside the laser cavity. The spectra have been fit to a sum of two
Lorentzian lineshapes to give the linewidths and center frequencies of each of
the transitions. Plots of the linewidths vs. pressure at low RF power are
linear within experimental error with slopes of 6.08 ± 0.19 MHz/Torr and 6.05 ±
0.19 MHz/Torr for the ground state and v_6 = 1 state transitions, respectively.

Further increase in pressure causes the upper state transition to disappear
and changes the sign of the intensity of the lower state transition. The
observed effects are not adequately represented by calculations based on simple
three-level resonances. We have written a computer program to calculate the
double resonance effect in a four-level system consisting of two coupled three-
level systems and have obtained much better agreement between observed and
calculated spectra. Lineshapes predicted by the new program will be compared to
experimental spectra.

Address of Fawzy and Schwendeman: Department of Chemistry, Michigan State
University, East Lansing, MI 48824.

RC1.   (8:30)

VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF FOUR DISTINCT CONFORMATIONAL STATES
OF POLY(L-LYSINE) IN AQUEOUS SOLUTION

M.G. PATERLINI, T.B. FREEDMAN AND L.A. NAFIE

Fourier transform infrared vibrational circular dichroism spectra in the
amide I' region of poly(L-lysine) in D_2O solutions have confirmed the exis-
tence of three distinct conformational states and an unordered state in this
homo-polypeptide, each with a unique, characteristic VCD spectrum. The
right-handed α-helix gives rise to a (-+-) VCD pattern, the antiparallel
β-sheet to two strong negative features, and the extended helix (formerly
denoted the random coil) to a (+-) VCD couplet, for the amide I' vibrations.
In addition, a completely unordered conformation can be obtained which is
characterized by the absence of any amide I' VCD. The negative VCD in the
β-sheet conformation is interpreted in terms of vibrationally generated ring
currents.

Examples of amide I' VCD spectra for several proteins with known confor-
mational composition shows that these characteristic VCD patterns can also be
observed in complex systems.

Address: Department of Chemistry, Syracuse University, Syracuse, NY 13244-1200

RC2.   (8:47)

VIBRATIONAL CIRCULAR DICHROISM OF TARTARIC ACID ESTERS. CONFIGURATIONAL
CORRELATION AND UNIQUE SENSITIVITY TO HYDROGEN BONDING EFFECTS

T. CHANDRAMOULY, C. S. EWIG AND P. L. POLAVARAPU

Vibrational circular dichroism (VCD) in tartaric acid, dimethyl tartrate, diethyl tartrate and diisopropyl tartrate
have been measured in CCl_4 and DMSO solvents. These measurements, which are in addition to those reported
earlier,[1] inidicate that the VCD associated with C^*-O stretching vibrations is identical in all the molecules of the
present series. However, VCD associated with the C=O stretching vibration differs from molecule to molecule.
These differences are attributed to the well known internal hy   gen bonding and the influence there on from the
substituents in COOR group. In order to get a physical pictur   the different possible hydrogen bonded
conformers, ab initio calculations have been carried out ar ' ne minimum energy conformers are identified. The
conclusions emerging from these studies point to the extreme sensitivity of VCD, associated with the C=O
stretching vibrations, to the nature of internal hydrogen bonding

[1]P. L. Polavarapu, '40th Symposium on Molecular Spectroscopy,' Columbus, OH (1985). Paper WE3

Address of Chandramouly, Ewig and Polavarapu: Department of Chemistry, Vanderbilt University, Nashville,
TN 37235

RC3. (9:04)

THE VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF 2-METHYLOXETAN AND 3-METHYLOXETAN-2,2-D$_2$

R.A. SHAW, N. IBRAHIM, AND H. WIESER

The VCD spectra of the title compounds are reported in the region of 1600-800 cm^{-1}. The 3-21G harmonic *ab initio* force fields are determined by adjusting scaling factors to fit the observed infrared absorption and Raman spectra of the title compounds and several deuterated analogs. The VCD and infrared absorption intensities are obtained using the resulting force fields in conjunction with the fixed partial charge model. Discrepancies between observed and calculated intensities are rationalized in terms of vibrationally induced charge redistribution (charge flow) in certain modes.

Address: Department of Chemistry, University of Calgary, Calgary, Alberta, T2N 1N4 Canada.

RC4. (9:21)

VIBRATIONAL CIRCULAR DICHROISM OF AMINO ACIDS AND OLIGOPEPTIDES AS A FUNCTION OF SOLUTION pH

W. M. ZUK, A. N. SCANGAS, T. B. FREEDMAN, AND L. A. NAFIE

VCD spectra in the C-H stretching and C-H bending regions for selected amino acids, dipeptides, and tripeptides at various pH values will be presented. The changes observed in the VCD of these small biological molecules in aqueous solution as a function of pH support the recently proposed ring current mechanism of VCD. It is proposed that electronically generated ring current loops closed by intramolecular hydrogen bonding within many types of molecules results in enhanced VCD intensities. The alteration of the pH of solutions of amino acids and small peptides apparently disrupts this intramolecular hydrogen bonding. Further evidence of the ring current mechanism will be demonstrated through examination of these effects.

Address: Department of Chemistry, Syracuse University, Syracuse, New York 13244.

RC5. (9:38)

BOND-POLARIZABILITY RAMAN OPTICAL ACTIVITY CALCULATIONS OF (S)-(-)-EPOXYPROPANE AND COMPARISON TO EXPERIMENT.

JUAN R. ESCRIBANO AND LAURENCE D. BARRON

A revision of the bond-polarizability theory of Raman optical activity (ROA) has been carried out and applied to (S)-(-)-epoxypropane. This molecule is particularly interesting because a force field has been attempted, all its bonds are axially symmetric and the depolarized ROA spectrum is published. The correlation obtained does not match all Δ_z experimental values but seems reasonable considering the quality of the theoretical data (force constants and electrooptic parameters).

Address of J.R. Escribano: Department of Chemistry, Syracuse University, Syracuse, NY 13244-1200

Address of L.D. Barron: Department of Chemistry, The University, Glasgow G12 8QQ UK

RC6.

FOURIER TRANSFORM INFRARED VIBRATIONAL CIRCULAR DICHROISM OF MATRIX ISOLATED MOLECULES

D. O. HENDERSON AND P. L. POLAVARAPU

Vibrational circular dichroism (VCD) of matrix isolated molecules in the 3100-2800 cm^{-1} region has been reported by Stephens and coworkers[1] using a dispersive VCD instrument. We will discuss the feasibility of VCD measurements of matrix isolated molecules in the 1650-800 cm^{-1} region using an FTIR spectrometer. The details of techniques employed and the VCD spectra, at 1 cm^{-1} resolution of (+)-α-pinene in Ar and N$_2$ matrices will be presented.

[1] D. W. Schlosser, F. Devlin, K. Jalkanen and P. J. Stephens, Chem. Phys. Lett., 88, 286 (1982).

Address of Henderson and Polavarapu: Department of Chemistry, Vanderbilt University, Nashville, TN 37235

RC7.

VIBRATIONAL CIRCULAR DICHROISM IN TRANSITION METAL COMPLEXES. RING CONFORMATION AND RING CURRENTS

T.B. FREEDMAN, D.A. YOUNG AND L.A. NAFIE

The vibrational circular dichroism (VCD) spectra of tris complexes of Co(III) with ethylenediamine, β-alanine and α-amino acid ligands have been investigated. Monosignate VCD features in the NH and CH stretching regions and CH bending region are attributed to magnetic dipole transition moments arising from oscillating electric current in the chelate ring or in rings closed by direct hydrogen bonding or anion bridging between ligands. The currents are generated by hydrogen stretching or bending motion adjacent to or within the rings.

The analyses of the VCD spectra lead to qualitative and in some cases quantitative determination of the solution conformation of the five or six membered chelate rings. The VCD of the amino acid complexes is consistent with chelate rings which are puckered in such a way to permit the maximum extent of N-H$\cdots$O=C hydrogen bonding (σ or π) between adjacent ligands. For the ethylenediamine complex, the addition of excess chloride ion results in a structure of D$_3$ symmetry with three Cl$^-$ bridges between NH$_2$ groups and all ethylenediamine rings in the lel conformation.

Address: Department of Chemistry, Syracuse University, Syracuse, NY 13244-1200

RC8.

A LOCAL MODE THEORY FOR VIBRATIONAL ABSORPTION AND CIRCULAR DICHROISM

P. L. POLAVARAPU

Simple molecules of the type A$_2$B$_2$ with C$_2$ symmetry are considered to investigate the relation of vibrational absorption and circular dischroism (VCD) to the molecular chirality. Symmetry arguments, a local mode concept and Sayvetz conditions are used to derive the Cartesian displacements for symmetric and antisymmetric stretching vibrations. Further, simple expressions are derived for the absorption and VCD intensities of these two stretching modes. It is shown that for these two modes in addition to VCD being characteristic with bisignate (equal intensity) bands, the absorption intensities are also characteristic with a simple realtion. Further, the relation of coupled oscillator type concepts to those that include charge reorganization contribution to VCD became clear from the equations derived.

Address of Polavarapu: Department of Chemistry, Vanderbilt University, Nashville, TN 37235

RC9.   (10:49)

VIBRATIONAL CIRCULAR DICHROISM AS A CRITERION FOR LOCAL MODE VERSUS NORMAL MODE BEHAVIOR

S. ABBATE, G. LONGHI, L. RICHARD, C. BERTUCCI, C. ROSINI, P. SALVADORI, AND A. MOSCOWITZ

The local mode approach frequently permits a straightforward and appealing interpretation of near infrared and visible vibrational spectra of the higher overtones of organic molecules.[1] Vibrational circular dichroism (VCD) spectra have the potential to distinguish readily between local mode and normal mode behavior. This is so because the kinetic and potential energy couplings that lead to normal mode behavior are frequently crucial for the generation of significant VCD intensity. To test this concept, we have undertaken a VCD study in the spectral region 1000-800 mμ of terpenes and related molecules. The molecules are of the sort whose VCD spectra have been studied extensively in the CH-stretching fundamental region by Laux et al.[2] The concept seems to be a useful one. For example, we find that (R)-(+)-limonene and its enantiomer exhibit circular dichroism for the third overtone that can be attributed to normal modes of the sort discussed in reference 2; on the other hand, we can detect no VCD intensity in the analogous transition of (-)-menthone.

[1] B. R. Henry, in "Vibrational Spectra and Structure," J. R. Durig, Ed.; Elsevier; New York, 1981; Vol. 10.

[2] L. Laux, V. M. Pultz, S. Abbate, H. A. Havel, J. Overend, A. Moscowitz and D. A. Lightner, J. Am. Chem. Soc. 104, 4276 (1982).

Address of Abbate: Istituto di Chimica delle Macromolecole, C.N.R., Milano, Italy.

Address of Longhi: Dipartimento di Chimica Industriale, Politecnico, Milano, Italy.

Address of Richard: Laboratoire de Spectroscopie Infrarouge, Bordeaux, France.

Address of Bertucci, Rosini and Salvadori: Centro Studi C.N.R. delle Molecole stereoordinate e otticamente attive, Pisa, Italy.

Address of Moscowitz: Chemistry Department, University of Minnesota, Minneapolis 55455, Minnesota.

RC10.   (11:06)

ROTATIONAL OPTICAL ACTIVITY

P. L. POLAVARAPU

Optical activity generated by the rotational normal coordinates is investigated. The theoretical formulation is based on classical principles and uses the definition of the rotational normal coordinates and the changes in electric and magnetic dipole moment components along the principal axes of inertia due to rotations represented by these coordinates. The resulting expressions indicate that rotational circular dichroism (CD) is supported by chiral asymmetric top molecules whereas rotational Raman optical activity (ROA) is supported by the chiral asymmetric top and as well as symmetric top molecules. For a two group molecule of C_2 symmetry, rotations around the two principal axes perpendecular to C_2 axis are noted to generate opposite signed CD. Also opposite signed ROA is predicted for these rotations in a two group molecule.

Address of Polavarapu: Department of Chemistry, Vanderbilt University, Nashville, TN 37235

RC11.   (11:23)

VIBRATIONAL ABSORPTION AND CIRCULAR DICHROISM STUDIES ON CARBOHYDRATES

D. M. BACK AND P. L. POLAVARAPU

Vibrational circular dichroism (VCD) of simple carbohydrates have been measured in the 1600-800 cm^{-1} region. Various configurational correlations are found. In order to understand these correlations with the nature of vibrations that are associated with VCD features, time dependent absorption spectra of parent and deuterated glucose molecules and a few other carbohydrates were investigated. Also the geometries and force constants for α and ß glucose anomers were investigated using CNDO molecular orbital theory.

Address of Back and Polavarapu: Department of Chemistry, Vanderbilt University, Nashville, TN 37235

RC12.   (11:40)

Extension of VCD measurements towards the far IR

Günter Georg Hoffmann

First experience with a new, laboratory build photo-

elastic modulator is presented. The device uses an

optical element which is transmittand down to 300/cm.

Infrared CD spectra of (+)-3-methylcyclohexanone and

some other substances of interest to VCD spectrosco-

pists are shown and discussed.

Address: Lehrstuhl für Physikalische und Theoretische Chemie,
            Universität Essen, Gesamthochschule, D-4300 Essen 1,
            West Germany.

RC13.   (11:52)

VIBRATIONAL CIRCULAR DICHROISM OF SUBSTITUTED ALLENES

T.A. KEIDERLING, U. Narayanan, J.S. Chickos, W. Runge and C.J. Elsevier

The infrared spectra of 1,3-dideutero allene in the vapour phase and Raman spectra of the neat liquid were obtained. The fundamental frequencies were assigned and the force field for allene calculated using allene-d_0, allene-1,1,-d_2, allene-d_4, allene-d_1, and allene-1,3-d_2. For several substituted allenes we have measured the VCD in the C-H stretching, C=C=C assymetric stretching and bending regions. For the simplest substituted, chiral, 1-methyl, 3-haloallenes we have calculated the dipolar and rotational strengths using both an empirical transfered force field and a semi-empirical CNDO/2 force field, with the FPC and LMO models of VCD. The data indicates a qualitative agreement between theory and experiment for non overlapping bonds.

Address of T.A. Keiderling and U. Narayanan: Chemistry Department, University of Illinois at Chicago, Box 4348, Chicago, Illinois 60680.

MILLIMETER WAVE SPECTRUM OF THE NS FREE RADICAL
IN ITS SIX FIRST VIBRATIONAL STATES

J. ANACONA. P.B. DAVIES. M. BOGEY. C. DEMUYNCK and J.L. DESTOMBES

The millimeter wave spectrum of NS $(X^2\Pi)$ in the vibrational states $v \leq 5$ has been investigated. The free radicals are created and observed inside a R.F. discharge in N_2 + H_2S mixtures. The experimental data are fitted together in a least-squares procedure. in order to determine the vibrational dependance of the molecular parameters.

Address of Anacona and Davies : Department of Physical Chemistry. University of Cambridge. Lensfield road - Cambridge CB2 1EP - U.K.

Address of Bogey. Demuynck and Destombes : Université de Lille. Laboratoire de Spectroscopie Hertzienne. associé au CNRS - F 59655 Villeneuve d'Ascq Cedex - FRANCE.

MICROWAVE STUDIES OF SMALL CLUSTERS IN THE Ar/HF SYSTEM*

C. CHUANG, T. D. KLOTS, T. EMILSSON, AND H. S. GUTOWSKY

Expansion of an Ar/HF gas mixture from a supersonic nozzle generates a progression of small clusters Ar_n, $(HF)_m$ and $Ar_n(HF)_m$. Of these, the Ar-HF and $(HF)_2$ dimers were among the first weakly bonded complexes to be detected and characterized by rotational spectroscopy. More recently, we have reported preliminary observations of Ar_2-HF, a T-shaped trimer,[1] and of Ar_3-H/DF, a symmetric top tetramer,[2] with the Flygare-Fourier transform microwave spectrometer. These and subsequent results for the Ar/HF system will be presented.

Over 20 b-dipole transitions have now been observed in the 4-18 GHz region for both Ar_2-HF and Ar_2-DF, and their hyperfine structure analyzed. Fitting of the line centers for Ar_2-DF with Kirchoff's NBS program[3] gives A'', B'', and C'' rotational constants of 3 506.745(1), 1 744.094(1) and 1 144.478(1) MHz and centrifugal distortion constants (assuming planarity) of -38(1), -0.49(1), and -178(3) kHz for τ_{bbcc}, τ_{ccaa}, and τ_{aabb}. The significance of these and similar results for Ar_2-HF will be discussed. Analysis of the hyperfine structure shows that the torsional oscillations of the H/DF are anisotropic. For Ar_2-HF the average in-plane amplitude is 32.8° and the out-of-plane, 29.7°.

A sizeable number (~50) of as yet unassigned lines have been found for the Ar/HF system. Most likely they are from other small clusters such as $Ar-(HF)_2$, $Ar_2-(HF)_2$, and Ar_4-HF. Further efforts are in progress to identify the clusters involved, including a search specifically for Ar_4-HF. Any new results, or lack of them, will be reported.

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[1] H. S. Gutowsky, T. D. Klots, C. Chuang, C. A. Schmuttenmaer, and T. Emilsson, J. Chem. Phys. 83, 4817 (1985).
[2] H. S. Gutowsky, T. D. Klots, C. Chuang, J. D. Keen, C. A. Schmuttenmaer, and T. Emilsson, J. Am. Chem. Soc. 107, 7174 (1985).
[3] W. H. Kirchoff, J. Mol. Spectros. 41, 333 (1972).

Address: Noyes Chemical Laboratory, University of Illinois, Urbana, IL 61801.

RD3.

ROTATIONAL SPECTRA AND STRUCTURES OF SMALL CLUSTERS: Ar_2-HCl AND Ar_3-HCl*

T. D. KLOTS, R. S. RUOFF, C. CHUANG, AND H. S. GUTOWSKY

Microwave rotational spectra have been observed for the small clusters Ar_2-$H^{35}Cl/^{37}Cl$ and Ar_3-$H^{35}Cl/^{37}Cl$. The hyperfine structure of the transitions has been analyzed and the chlorine quadrupole coupling and the line centers determined. The line centers were used to obtain the ground state rotational constants.

The trimeric cluster, Ar_2-HCl, has an equilibrium, T-shaped structure with the H pointed at the Ar_2 midpoint. The values of A, B, and C determined for the ^{35}Cl species with the Kirchoff program[1] are 1 733.857, 1 667.932, and 844.492 MHz; τ_{aaaa}, τ_{bbbb}, τ_{aabb}, and τ_{abab} are -120, -80, 41, and -65 kHz. The quadrupole coupling constants χ_{aa} and $\chi_{bb-\chi_{cc}}$ are -28.11 and -3.18 MHz. A value of 3.828 Å is found for the Ar-Ar interatomic distance.

The Ar_3-HCl is a symmetric top with the H of the HCl pointing towards the Ar_3. The spectroscopic constants for the ^{35}Cl version are B_0 = 843.897 MHz, D_J = 2.33 kHz, D_{JK} = 1.82 kHz, and χ_{aa} = -30.006 MHz. By combining B_0 for the $H^{37}Cl$ complex (825.981 MHz) with that for $H^{35}Cl$, we find the Ar-Ar distance in Ar_3 to be 3.852 Å.

Several aspects of the results will be considered: The longer Ar-Ar distance in Ar_3 than in Ar_2. A comparison of results for the HF and HCl containing clusters. The dependence of the average torsional angle for the HX upon size of the Ar_n (n = 1,2,3), as determined from the hyperfine interactions. Use of the centrifugal distortion to obtain some insight concerning the weak van der Waals interactions and vibrational modes.

[1]W. H. Kirchoff, J. Mol. Spectros. 41, 333 (1972).

Address: Noyes Chemical Laboratory, University of Illinois, Urbana, IL 61801.

RD4.

ROTATIONAL SPECTROSCOPY OF SMALL CLUSTERS WITH A FLYGARE FOURIER TRANSFORM MICROWAVE SPECTROMETER*

T. EMILSSON AND H. S. GUTOWSKY

The Flygare-Balle microwave spectrometer[1] has been very useful in the study of hydrogen bonded and van der Waals dimers. Recently we have been able to extend its application to the study of trimers and tetramers such as Ar_2-HX, Ar_3-HX, and $(HCN)_3$. Detection and characterization of other small clusters seem feasible. This has been made possible by a continuing series of practical refinements in the Mark II Flygare spectrometer.[2]

They include the following: (a) The cavity is used in a reflection mode rather than in transmission.[3] This arrangement permits much better recovery of the molecular signal, resulting in a sensitivity improvement from 2 to more than 100-fold depending on frequency. (b) Externally adjustable skimmer slits have been installed, permitting almost complete elimination of Doppler broadening, at a modest sacrifice of signal strength. (c) A sample preparation system has been devised which allows precise fingertip control of the sample composition and pressure. The stock gases are handled through capillary Teflon tubes and diluted to the desired concentration with carrier gas only two seconds before being pulsed into the spectrometer. This permits quick and easy optimization of sample composition and eliminates the problem of adsorption and isotope exchange with plumbing walls.

[1]T. J. Balle, E. J. Campbell, M. R. Keenan, and W. H. Flygare, J. Chem. Phys. 71, 2723 (1979).
[2]E. J. Campbell, W. G. Read, and J. A. Shea, Chem. Phys. Lett. 94, 69 (1983).
[3]T. J. Balle and W. H. Flygare, Rev. Sci. Instr. 52, 1 (1981).

Address: Noyes Chemical Laboratory, University of Illinois, Urbana, IL 61801.

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MICROWAVE AND MICROWAVE-MICROWAVE DOUBLE RESONANCE SPECTROSCOPY OF
TORSIONALLY EXCITED METHYL FORMATE

GRANT M. PLUMMER, ADAM WALTERS, AND JOHN G. BAKER

Initial measurements of the rotational transition frequencies of methyl
formate in its first excited torsional state will be presented. In this
work, standard Stark spectroscopy in the 11-28 GHz range has been augmented
by the use of microwave-microwave double resonance spectroscopy, which aids
in the location and assignment of rotational transitions belonging to the
same torsional state. Computational methods will be discussed as well.

Address of Plummer: I. Physikalisches Institut, Universität zu Köln, Zül-
picher Strasse 77, 5000 Köln 41 Fed. Republic of Germany.
Address of Walters and Baker: Schuster Laboratory, University of Manchester,
Manchester M13 9PL England.

DIRECT OBSERVATION OF TORSIONAL LEVELS AND VIBRATION-TORSION-ROTATION INTERACTION IN RAMAN
SPECTRA OF C_2H_6

R. FANTONI[**], K. van HELVOORT[*], W. KNIPPERS[*], J. REUSS[*] and W.L. MEERTS[*]

The detection of spontaneous Raman scattering induced by an intense Ar ion laser in an
intracavity cell containing C_2H_6 (either bulk or jet) has allowed the measurement of weak
bands involving the excitation of the torsional mode ν_4. Barrier induced splittings have been
measured up to the fifth torsional level. Current theories for vibrational-torsional-rotational
interaction in the case of a high barrier have been applied to interpret the Raman spectra.
The calculated ν_4 energy levels used in the simulation give a qualitative picture of the
spectra. Quantitative agreement has been found up to the third overtone by choosing $V_3=1009.1$
cm^{-1} and $V_6=11.0$ cm^{-1}. Measurement of $2\nu_9+2\nu_4$, $2\nu_6+2\nu_4$ and $2\nu_2+2\nu_4$ combination bands has
given information on the effect of the molecular vibrations on the torsional barrier. New
results on CH_3CD_3 will be presented as well.

[*]Fysisch Laboratorium, Katholieke Universiteit Nijmegen, Toernooiveld, 6525 ED Nijmegen,
The Netherlands
[**]Permanent address: Lab. Spettroscopia Molecolare ENEA, CRE Frascati, Italy

RD'1.   (10:15)

OBSERVATION OF CALCIUM AND STRONTIUM MONOALKYLAMIDES AND
A ROTATIONAL ANALYSIS OF SrNH$_2$

C. R. BRAZIER, A. M. R. P. BOPEGEDERA and P. F. BERNATH

The reaction of Ca and Sr vapor with monoalkylamines in a Broida type oven yields the corresponding monoalkylamides MNHR (M=Ca or Sr ; R=H,CH$_3$,C$_2$H$_5$,C$_3$H$_7$,C$_4$H$_9$). The electronic and vibrational structure of the different species will be described and compared.

The $\tilde{B}^2B_1-\tilde{X}^2A_1$ transition of SrNH$_2$ has been analysed at Doppler-limited resolution. rNH$_2$ is a planar very near prolate asymmetric top (k=-0.9993). The $\tilde{B}-\tilde{X}$ transition has perpendicular structure complicated by a very large spin-rotation splitting in the upper state (E_{aa}=-34cm^{-1}) due to the interaction with the nearby $\tilde{A}^2B_2$ state. A description of the spectra will be presented together with an analysis of the results.

Address of Brazier Bopegedera and Bernath: Department of Chemistry, University of Arizona, Tucson AZ 85721.

RD'2.   _   (10:32)

ORGANOMETALLIC FREE RADICALS: OBSERVATION OF OPEN-FACED SANDWICH COMPLEXES OF ALKALINE EARTH METALS

L. ELLINGBOE, C. BRAZIER, D. BOPEGEDERA AND P. BERNATH

We have discovered that calcium and strontium vapors react with cyclopentadiene and pyrrole. The reaction of M with C$_5$H$_6$ produces the MCp (M=Ca, Sr; Cp=C$_5$H$_5$) free radical of C$_{5v}$ symmetry. Two electronic transitions $\tilde{B}^2A_1-\tilde{X}^2A_1$ and $\tilde{A}^2E_1-\tilde{X}^2A_1$ were assigned by analogy with the corresponding alkaline earth monohalide and monohydroxide spectra. Similar spectra were observed when pyrrole (C$_4$H$_5$N) was used as an oxidant instead of cyclopentadiene.

Address of Ellingboe, Brazier, Bopegedera and Bernath: Department of Chemistry, University of Arizona, Tucson, Arizona 85721.

RD'3. (10:49)

LIFETIME MEASUREMENTS OF THE INDIVIDUAL MOLECULAR EIGENSTATES OF THE PERTURBED J'=0 LEVELS OF THE $^1B_{3u}$ STATE OF PYRAZINE

W.M. van HERPEN[*], W.L. MEERTS[*], K.E. DRABE[**] and J. KOMMANDEUR[***]

The lowest excited singlet $^1B_{3u}$ state of pyrazine is known to be coupled to a number of triplet $^3B_{3u}$ states. Using a strongly collimated molecular beam and a single frequency laser it is shown that the J'=0 of the 0_0^0 transition contains at least 36 states. We have individually excited 8 of these states and studied their decay. The lifetimes found (typically 450 ns) do not scale with the intensities of the excitation spectrum. This deviation is caused by a non-radiative decay of the zero order $^3B_{3u}$ states. With a simple model it was possible to reconstruct the absorption spectrum, the energies of the zero order states and its coupling strengths. The zero order decay rates of the singlet and triplet states have been determined. The values obtained for the zero order singlet state is 5.4 MHz; the values for the triplet states range from 0.6 to about 5.0 MHz.

[*]Fysisch Laboratorium, K.U. Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

[**]Physical Chemical Laboratory, V.U. Amsterdam, de Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

[***]Laboratory for Physical Chemistry, University of Groningen, Nijenborgh 16, 9747 AC Groningen, The Netherlands

RD'4. (11:06)

The Optical Spectrum of NO_2: Spectral Ergodicity without Level Repulsion
Kevin K. Lehmann, Stephen L. Coy, and John P. Pique

We have performed microwave-optical double resonance measurements to determine the absorption spectrum from a number of rotational levels of the ground state of NO_2. These experiments demonstrate that the eigenstates observed in absorption in the spectral region near 17,000 cm^{-1} are almost ideal ergodic mixtures of basis functions with different values of vibronic and K_a quantum numbers. By observing spectra from lower states differing in J by 2, we have obtained branch assignments for about 300 upper states. The energy level spacing statistics looked almost perfectly Poisson, not the Wigner statistics expected for a strongly mixed quantum spectrum. An independent test of the level spacing statistics, which does not require splitting the spectrum up into P and R branches, also indicated that the spectrum has Poisson statistics.

The implication of this result for our understanding of "quantum chaos" will be discussed.

Lehmann: Department of Chemistry, Princeton University
Coy: Department of Chemisty, Harvard University
Pique:Department of Chemistry, M.I.T.

RD'5.

THE FLUORESCENCE AND PHOSPHORESCENCE EXCITATION SPECTRA OF JET COOLED ACETOPHENONE [1]

J. L. TOMER, K. W. HOLTZCLAW, L. H. SPANGLER, AND D. W. PRATT

We have obtained both the fluorescence and phosphorescence excitation spectra of aceto-phenone in the collision-free environment of a supersonic jet in order to probe the potential energy surfaces of the lowest excited singlet and triplet states. A comparison of these two spectra reveals, even at the level of vibrational resolution, that the equilibrium geometries of the two states are quite different. An analysis of these results will be given, possible reasons for these differences will be discussed, and a preliminary interpretation of the par-tially resolved rotational structure in these spectra will be presented.

Address of Tomer, Holtzclaw and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.
Address of Spangler: MS-G738, LANL, Los Alamos, NM 87545.

RD'6.

ROTATIONALLY RESOLVED FLUORESCENCE EXCITATION SPECTRUM OF STILBENE [1]

W. M. VAN HERPEN, W. L. MEERTS, M. V. RAMAKRISHNA, AND D. W. PRATT

Well-resolved rotational structure, limited only by the radiative lifetime of the electronically excited state, has been observed in the fluorescence excitation spectra of stilbene and stilbene-Ar van der Waals complexes using a highly collimated molecular beam and a single frequency dye laser. A preliminary analysis of this structure, giving infor-mation about the equilibrium geometries of ground and excited states, will be given. We will also describe the dependence of this structure, in the free molecule, on the excess vibrational energy in the excited state, and comment on the relation of this dependence to the problem of photoisomerism in stilbene.

Address of van Herpen and Meerts: Fysisch Laboratorium, K. U. Nijmegen, 6525 ED Nijmegen, The Netherlands.
Address of Ramakrishna and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

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RE1.   (1:30)

HYDROGEN MIGRATION TUNNELING EFFECTS IN THE INFRARED SPECTRUM OF PROTONATED ACETYLENE $C_2H_3^+$

JON T. HOUGEN

The goal of the present work is to indicate what sorts of rotation-vibration spectra might be expected for protonated acetylene when the three protons in the molecule are allowed to interchange roles in a cyclic manner by migrating around an elliptical orbit enclosing the two carbon atoms, as suggested by ab initio calculations[1,2].
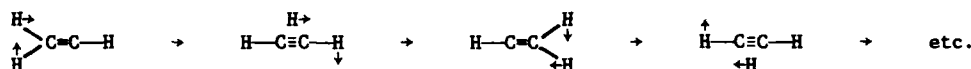
On the one hand, approximate rotation-vibration-tunneling energy levels can be obtained by mapping the protonated acetylene problem onto an internal rotation problem already discussed in the literature[3] in terms of numerical calculations in a Principal-Axis-Method treatment. On the other hand, semi-quantitative rotation-vibration-tunneling energy levels can be obtained for the high barrier limit by applying to protonated acetylene an Internal-Axis-Method-like formalism originally set up to treat the water dimer. The agreement betwen the numerical PAM calculations and the algebraic IAM results serves as a check on both.

Unfortunately, the development of this formalism, with its tunneling splittings, statistical weights, selection rules, etc., has not yet led to an assignment of the spectrum of $C_2H_3^+$ reported last year at this meeting by Crofton and Oka[4].

[1]J. Weber, M. Yoshimine and A. D. McLean, J. Chem. Phys. **64**, 4159-4164 (1976).
[2]G. P. Raine and H. F. Schaefer III, J. Chem. Phys. **81**, 4034-4037 (1984).
[3]E. B. Wilson Jr., C. C. Lin and D. R. Lide, J. Chem. Phys. **23**, 136-142 (1955).
[4]M. W. Crofton and T. Oka, Columbus Symposium Abstracts 1985, TE13.

Address of Hougen: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

RE2.   (1:47)

ROTATION-VIBRATION ENERGIES OF PROTONATED ACETYLENE $C_2H_3^+$

R. ESCRIBANO AND P.R. BUNKER

Ab initio studies predict that protonated acetylene has two possible equilibrium structures separated by a low barrier. The potential function can be expressed in terms of an angle that describes the rotation of the three H atoms around the C-C core, and it features two alternating sets of minima corresponding to either possible structure, with a $\pi/6$ periodicity.

We have applied the semirigid bender model, with the necessary modifications for a periodic potential, to study the rotation and 'internal rotation' energy levels of this ion, and the variation with the energy difference and barrier height between the two structures.

Address: Herzberg Institute of Astrophysics, National Research Council, Ottawa, Ontario, Canada K1A 0R6.

RE3.   (2:04)

THE PUZZLING INFRARED SPECTRUM OF A CARBONIUM ION ($C_2H_3^+$?)

M.W.CROFTON, B.D.REHFUSS, B.M.DINELLI and T.OKA

A complicated carbonium ion spectrum which is likely due to protonated acetylene was found in the 3 region last year[1] in the discharge of $He:H_2:C_2H_2$ (700:20:1). Several experiments have been done in an attempt to eliminate the possibility that the spectrum is due to other molecular ions. These have so far reinforced our conviction that the spectrum is indeed due to protonated acetylene. The assignment and analysis of the spectrum, however, has not been possible despite the existence of clear series of R and P branch lines and the approximate appearance of an assymetric rotor pattern. This is probably due to the existence of two isomeric structures (classical and non-classical) which may interconvert because of their similar energy and small barrier to conversion.[2] The very recent theoretical work by Hougen[3] and Lee and Schaefer[4] have direct be ring on this problem. We describe our experimental effort to unravel this fascinating puzzle.

[1]Paper TE13, 1985 Symposium on Molecular Spectroscopy, Ohio State University.
[2]J.Weber, M.Yoshimine and A.D.McLean, JCP 64, 4159 (1976).
[3]Jon Hougen, to be published.
[4]T.J.Lee and H.F.Schaefer III, to be published.

Address of Authors: Department of Chemistry and Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637.

RE4.   (2:21)

ANALYSIS OF THE ν_2 BAND OF D_3^+

S. C. FOSTER, A. R. W. McKELLAR, AND J. K. G. WATSON

Earlier ion-beam measurements[1,2] of the ν_2 band of the D_3^+ ion have now been supplemented with gas absorption measurements using diode laser sources and a cooled hollow-cathode discharge cell.   At least 80 lines have been assigned and fitted using an effective Hamiltonian with a Padé representation of the centrifugal distortion effects[3]   These fits will be compared with others that include vibrationally off-diagonal interactions explicitly.

[1]J.-T. Shy, J. W. Farley, W. E. Lamb, Jr., and W. H. Wing, Phys. Rev. Lett. 45, 535 (1980).
[2]J.-T. Shy, Ph. D. dissertation, University of Arizona (1982).
[3]J. K. G. Watson, S. C. Foster, A. R. W. McKellar, P. Bernath, T. Amano, F. S. Pan, M. W. Crofton, R. S. Altman, and T. Oka, Can. J. Phys. 62, 1875 (1984).

Address of Foster: Department of Chemistry, The Ohio State University, Columbus, OH 43210.
Address of McKellar and Watson: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

RE5.   (2:33)

HIGH-J LINES IN THE ν_2 BAND OF H_3^+

W. A. MAJEWSKI, M. D. MARSHALL, A. R. W. McKELLAR, AND J. K. G. WATSON

This paper reports on the analysis of the high-J emission lines of the ν_2(e') band of H_3^+ described at last year's Symposium, together with new absorption measurements using diode laser sources and the same type of hollow-cathode cell that have confirmed some of the emission measurements and extended them to lower wavenumbers.   These high-J lines show clearly the effects of the perturbation of the ν_2(e') state by the ν_1(a$_1'$) state, even although the pure vibrational separation between them is about 650 cm^{-1}.   Fits of these data together with the lower-J lines[1], using both effective Hamiltonian and supermatrix models that include the (ν_1, ν_2) interaction explicitly, will be reported.

[1]J. K. G. Watson, S. C. Foster, A. R. W. McKellar, P. Bernath, T. Amano, F. S. Pan, M. W. Crofton, R. S. Altman, and T. Oka, Can. J. Phys. 62, 1875 (1984)

Address of Majewski: Department of Chemistry, University of Pittsburgh, Pittsburgh PA 15260.
Address of Marshall, McKellar, and Watson: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

RE6.

A MORSE OSCILLATOR ADAPTED ROTATION-VIBRATION HAMILTONIAN FOR H_3^+

PER JENSEN, V. SPIRKO, AND P.R. BUNKER

We have developed a Morse oscillator adapted rotation-vibration Hamiltonian for an equilateral triangular X_3 or X_2Y molecule for the purpose of calculating the rotation-vibration energies from the potential function in an efficient way.

In this paper we report the use of this Hamiltonian to calculate the rotation-vibration energies of H_3^+, H_2D^+, HD_2^+, and D_3^+ from an internuclear potential function. We have optimized the fit by adjusting the potential function, and we have found it necessary to allow for the breakdown of the Born-Oppenheimer approximation.

Address of Jensen: Department of Chemistry, University of Aarhus, Aarhus, Denmark.
Address of Spirko: Institute of Physical Chemistry, Czechoslovak Academy of Science, Prague, Czechoslovakia.
Address of Bunker: Herzberg Institute of Astrophysics, National Research Council, Ottawa, Canada.

RE7.

MEASUREMENT OF THE ν_4 VIBRATION OF AMMONIUM BY VELOCITY MODULATION DIODE LASER SPECTROSCOPY

M. POLAK, M. GRUEBELE, AND R.J. SAYKALLY

The triply degenerate bend (ν_4) of NH_4^+ has been studied by velocity modulation diode laser spectroscopy. 90 lines have been measured, about 30% of which have been assigned to low-J P and R branch transitions. Preliminary analysis yields a band origin of 1397 ± 1 cm^{-1}, and suggests strong Coriolis coupling between ν_2 and ν_4. A least squares fit to an effective spherical rotor Hamiltonian is in progress.

Address of Polak, Gruebele, and Saykally: Department of Chemistry, University of California, Berkeley, CA 94720.

RE8.

INFRARED SPECTRUM OF THE ν_3 BAND OF CH_3^+

M. W. CROFTON, M.-F. JAGOD, B. D. REHFUSS, W. A. KREINER, and T. OKA

We have observed[1] the vibration-rotation spectrum of the ν_3 band of CH_3^+. This ion was produced both in air-cooled and water-cooled discharge cells with a gas mixture of He : H_2 : CH_4 (700:20:1) with a total pressure of ≈ 7 Torr. The spectrum was observed using a difference frequency laser system combined with velocity modulation. The spectrum appeared in the same region as that of $C_2H_3^+$, but intensity variation with chemistry made it possible to discriminate lines of the two species.

About 150 lines have been measured and assigned. An extensive analysis was done using the symmetric rotor Hamiltonian with l-resonance and higher order effects, $i.e.$ $A_1 - A_2$ splitting. The spectral pattern clearly indicates that the geometrical structure of CH_3^+ has D_{3h} symmetry as anticipated by theory. The following preliminary fundamental vibration-rotation constants have been obtained (in cm^{-1}):

$\nu_0 + \frac{3}{4}\eta_k = 3106.53995(980)$	$B^0 = 9.36208(26)$	$C^0 = 4.61252$
	$B' = 9.27448(63)$	$C' = 4.56959 \qquad C'\zeta_{33} = 0.52025$

In separating $C'\zeta_{33}$ from C', we used a calculated inertial defect of $\Delta_o = 0.0535$ amu$Å^2$.

[1]Mark W. Crofton $et\ al.$, $J.\ Chem.\ Phys.$, 83, 3702 (1985).

Address of Crofton, Jagod, Rehfuss, and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637.

Address of Kreiner: Department of Physical Chemistry, University of Ulm, Ulm, Federal Republic of Germany.

RE9. (3:54)

ANALYSIS OF THE ν_3 INFRARED FUNDAMENTAL BAND OF H_2O^+ ($X\ ^2B_1$)

B. M. DINELLI, M. W. CROFTON and T. OKA

The H_2O^+ optical spectrum was detected first in the laboratory by Lew[1] and later in the tail of comet Kohoutec[2]. We have previously reported the observation by difference frequency spectrometer of the vibration-rotation infrared spectrum of H_2O^+ in the region 3100-3400 cm^{-1} using an A.C. glow discharge through He, H_2 and O_2 (100:1:1). The observed lines were assigned to the ν_3 vibration-rotation band of that molecular ion. The ν_1 band was not observable unlike the case of isoelectronic NH_2 radical for which the ν_1 transitions were reported to be much stronger than the ν_3 transitions.

The ground state molecular constants of Lew have been improved by including ground state combination differences from our data in the fit. A Watson reduced asymmetric rotor Hamiltonian, including the spin rotation interaction was used. The Coriolis interaction between the ν_1 and ν_3 vibrations has been included in the Hamiltonian to determine the excited state molecular constants for the first time.

[1] H. Lew, I. Heiber, *J. Chem. Phys.* , **58** , 1246 (1972)

[2] P.A. Wehinger, S. Wyckoff, G.H. Herbig, G.Herzberg, H. Lew, *Ap. J.* , **190** , L43 (1974)

Address of Dinelli, Crofton and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637

Permanent address of Dinelli: Istituto di Spettroscopia Molecolare del C.N.R., Bologna, Italy

RE10. (4:11)

MEASUREMENT OF THE 01^10-11^10 BENDING HOT BAND AND OTHER WEAK BANDS OF HCS^+ BY VELOCITY MODULATION LASER SPECTROSCOPY

N.H. ROSENBAUM, J.C. OWRUTSKY, E. KEIM, L.M. TACK, AND R.J. SAYKALLY

Previously, we have measured the ν_1 band of $HC^{32}S^+$ near 3140 cm^{-1} using velocity modulation laser spectroscopy with a color center laser in a $He/CO/H_2S$ discharge (1). It was noticed that between any two fundamental lines there appeared a number of small ion lines that also seemed to belong to HCS^+. Upon changing to an $Ar/CH_4/H_2S$ discharge conditions which enhanced and rotationally heated the HCS^+ signal somewhat, and with improved sensitivity of the velocity modulation spectrometer, we were able to achieve S/N of >50 on some of these small HCS^+ transitions. Three bands were observed, in which for the weakest band, transitions were measured to J=35. One band is clearly the 01^10-11^10 bending hot band, as the ℓ-type doublets observed indicate. Tentatively, the other two bands correspond to the ν_1 band of $HC^{33}S^+$ and $HC^{34}S^+$ in natural abundance, which should be a factor of ≈25 weaker than ν_1 band of $HC^{32}S^+$, and the 001-101 stretching hot band. However, other combination bands of HCS^+ that fall near the same frequency region must also be considered.

1. N.H. Rosenbaum, J.C. Owrutsky, L.M. Tack, and R.J. Saykally, J. Chem. Phys. **83**, 4845 (1985).

Address of Rosenbaum, Owrutsky, Keim, Tack, and Saykally: Department of Chemistry, University of California, Berkeley, CA 94720

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RE11. (4:23)

MEASUREMENT OF THE VIBRATION-ROTATION SPECTRUM OF THE AMIDE ANION BY VELOCITY MODULATION LASER SPECTROSCOPY

L.M. TACK, N.H. ROSENBAUM, J.C. OWRUTSKY, and R.J. SAYKALLY

The vibration-rotation spectrum of the amide anion (NH_2^-) has been measured from 2900-3300 cm^{-1}.(1) The symmetric stretching vibration (ν_1) and anti-symmetric stretching vibration (ν_3) have been assigned; the band origins are at 3121.930(10) and 3190.830(38), respectively. These frequencies are in close agreement with ab initio calculations.(2,3)

NH_2^- was generated in a gas discharge of 3 torr of pure ammonia and detected via infrared laser absorption using the ion specific velocity modulation technique.

1. L.M. Tack, N.H. Rosenbaum, J.C. Owrutsky, and R.J. Saykally, J. Chem. Phys, submitted.
2. T.J. Lee and Schaefer, J. Chem. Phys. 83, 1784 (1985).
3. P. Botschwina, J. Mol. Spec., in press.
4. C.S. Gudeman, R.J. Saykally, Ann. Rev. Phys. Chem. 35, 387 (1984).

Address of Tack, Rosenbaum, Owrutsky, and Saykally: Department of Chemistry, University of California, Berkeley, CA 94720.

RE12. (4:50)

VELOCITY MODULATION LASER SPECTROSCOPY OF VIBRATIONALLY EXCITED CF^+: DETERMINATION OF THE MOLECULAR POTENTIAL FUNCTION

M. GRUEBELE, M. POLAK, and R.J. SAYKALLY

The lowest six vibrational hot bands of CF^+ have been measured in a helium/C_2F_6 discharge by velocity modulation laser spectroscopy. A total of 56 transitions has been fit to a Dunham expansion for v=0-7, yielding the parameters: ω_e = 1792.6654(18) cm^{-1}, B_e = 1.7204176(75) cm^{-1}, Y_{20} = -13.22968(54) cm^{-1}, and D_0 = 62086(5) cm^{-1}. The rotational temperature of CF^+ in the plasma is near 650°K and the vibrational temperature is approximately 4500°K.

Address of Gruebele, Polak, and Saykally: Department of Chemistry, University of California, Berkeley, CA 94720.

RF1.   (1:30)

CURVILINEAR COORDINATE FORMULATION FOR THE VIBRATION-ROTATION-
LARGE AMPLITUDE INTERNAL MOTION INTERACTIONS WITH APPLICATION
TO THE WATER MOLECULE

YUHUA GUAN AND C. RICHARD QUADE

        A theory for vibration-rotation-large amplitude internal motion
interactions is developed using curvilinear coordinates for the vibra-
tional degrees of freedom. An essential feature to the theory is our
coordination of two transformations for the separation of vibration
from rotation and vibration from the LAM in zeroth order. Series ex-
pansion in the vibrational coordinates is used to obtain the full
vibration-rotation-LAM Hamiltonian. A Van Vleck perturbation scheme
is used to obtain the effective rotation-LAM Hamiltonian, H_R^{EFF}, for
the molecule in the nth vibrational state.

        The theory has been applied to calculating the energy levels
of the water molecule, treating the bending mode as a LAM. The vibra-
tion-rotation-LAM energy levels have been calculated using the Hoy-
Mills-Strey and Hoy-Bunker force constants and molecular geometry.
For the vibration-LAM energy levels in the zero angular momentum
state 1) our results using the HB force constants are better than the
results of Bunker and co-workers using the HBJ theory; and 2) our
results using the HMS force constants are better than the results from
the HMS vibration-rotation theory. For the rotational energy levels,
the HB force constants give better results than the HMS force constants
with our calculation. Further, for the J = 10 levels, our results
are 70% better than those of Bunker and co-workers using the HBJ
theory and the HB force constants.

Address: Department of Physics, Texas Tech University, Lubbock,
          Texas,   79409

RF2.   (1:37)

$H_2^{18}O$: THE (041) , (220) , (121) , (022) , (300) , (201) , (102) , and (003) INTERACTING STATES.
LINE INTENSITIES BETWEEN 9 500 AND 11 500 cm^{-1}

J.-P. CHEVILLARD, J.-Y. MANDIN, J.-M. FLAUD and C. CAMY-PEYRET

    The spectrum of an oxygen-18 enriched water vapor sample has been recorded, between
9 500 and 11 500 cm^{-1}, under a resolution of 0.01 cm^{-1}, with the Fourier transform spectro-
meter built by J. Brault at the National Solar Observatory (Kitt Peak, Arizona). Its
analysis has led to the determination of about 250 accurate rotational energy levels,
belonging to the eight interacting vibrational states of $H_2^{18}O$: (041) , (220) , (121) ,
(022) , (300) , (201) , (102) , and (003). Moreover, 635 line intensities belonging to the
$4 \nu_2 + \nu_3$, $2 \nu_1 + 2 \nu_2$, $\nu_1 + 2 \nu_2 + \nu_3$, $2 \nu_2 + 2 \nu_3$, $3 \nu_1$, $2 \nu_1 + \nu_3$, $\nu_1 + 2 \nu_3$, and $3 \nu_3$ bands have
been measured, with an average uncertainty of 6 % .

Address of Chevillard, Mandin, Flaud and Camy-Peyret : Laboratoire de Physique Moléculaire
et Optique Atmosphérique, CNRS, Bâtiment 221, Campus d'Orsay, 91405 Orsay Cedex, France.

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RF3. (1:49)

THE ν_2 BAND OF HDO : LINE POSITIONS AND INTENSITIES

C. CAMY-PEYRET, J.-M. FLAUD and A. MAHMOUDI

Using high resolution (0.005 cm^{-1}) Fourier tranform spectra, it has been possible to perform an extended analysis of the hybrid ν_2 band of HDO . Besides, more than 350 intensities of lines belonging to the A-type and B-type components have been measured. These intensities were very satisfactorily reproduced using an appropriate expansion of the transformed transition moment operator of the ν_2 band. Finally a complete list of line positions and intensities has been computed and should be useful for atmospheric applications.

Address of Camy-Peyret, Flaud and Mahmoudi : Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, Bâtiment 221 Campus d'Orsay, 91405 Orsay Cédex, France

RF4. (2:01)

Line Positions and Strengths of HDO and D$_2$O in the (010) and (020) - (010) bands
R.A. Toth

The measurements were obtained with a high resolution (0.005 cm^{-1}) Fourier transform spectrometer and the results cover the 900 - 1900 cm^{-1} region. Assignments were also made in the (010) band of HD^{18}O and D$_2^{18}$O. The line strengths were analyzed using the F-factor method.

Address: Jet Propulsion Laboratory
Mailstop 183-301
4800 Oak Grove Drive
Pasadena, CA 91109

RF5. (2:13)

TEMPERATURE DEPENDENCE OF N$_2$-BROADENED HALFWIDTHS OF H$_2$O

ROBERT R. GAMACHE and LAURENCE S. ROTHMAN

The temperature dependence of N$_2$-broadened halfwidths of water was studied for rotational vibrational transitions of atmospheric importance. The halfwidths were calculated using cutoff free theory[1] with Anderson-Tsao-Curnutte[2] interruption functions and trajectories correct to first-order-in-time[3]. The calculations were carried out for pure rotational transitions and for ν_2 transitions. The temperature dependence was calculated assuming the exponential form

$$\gamma(T_0)=\gamma(T) \left\{ \frac{T}{T_0} \right\}^n$$

The exponent n has been calculated for different rovibrational transitions and the calculations have been performed over the temperature range 200 K to 1000 K to be applicable to both atmospheric studies as well as hot sources. The trends in n, such as vibrational dependence, J dependence, etc., are examined and recommended values are given.

1. D. Korff and R. P. Leavitt, Phys. Lett. A 53, 351(1975); D. Robert and J. Bonamy, J.Phys.(Paris) 40, 923(1979); R. P. Leavitt and D. Korpf, J. Chem. Phys. 74, 2180(1981).
2. P. W. Anderson, Phys. Rev. 76, 647-661(1949); 80, 511-513(1950); C. J. Tsao and B. Curnutte, J. Quant Spectrosc. Radiat. Transfer 2, 41-91(1962).
3. R. R. Gamache and R. W. Davies, J. Mol. Spectrosc. 109, 283-299(1985).

Address of Gamache: University of Lowell Center for Atmospheric Research,
                    450 Aiken Street, Lowell, MA 01854.

Address of Rothman: Optics Division, Air Force Geophysics Laboratory,
                    Hanscom AFB, MA 01731.

RF6. (2:40)

DIODE LASER MEASUREMENTS IN THE ν_1 BAND OF $^{16}O_3$

M. A. H. SMITH, K. B. THAKUR, C. P. RINSLAND, V. MALATHY DEVI, AND D. CHRIS BENNER

Absolute intensities and pressure-broadening coefficients for several individual vibration-rotation lines in selected spectral intervals in the ν_1 band of ozone were determined from laboratory spectra recorded in the 1100-1150 cm^{-1} region with a tunable diode laser spectrometer system. Ozone was prepared from 99.98% ^{16}O-enriched oxygen samples by the silent electrical discharge technique. Air and nitrogen were used as the broadening gases. Self- and oxygen-broadened halfwidths were also determined for a few transitions. In addition, air- and nitrogen-broadened halfwidths at room temperature for a number of lines in the same band were determined from spectra at 0.005-cm^{-1} resolution recorded with the Fourier transform spectrometer system at the National Solar Observatory on Kitt Peak.

Address of Smith and Rinsland: Atmospheric Sciences Division, Mail Stop 401A, NASA Langley Research Center, Hampton, Virginia, 23665-5225.
Address of Thakur: Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio, 43210.
Address of Malathy Devi and Benner: Physics Department, College of William and Mary, Williamsburg, Virginia, 23185.

RF7. (2:52)

INTENSITIES AND SELF-BROADENING OF OZONE NEAR 5 μm

M. A. H. SMITH, V. MALATHY DEVI, C. P. RINSLAND, AND D. CHRIS BENNER

A series of high-resolution (0.005 cm^{-1}) spectra of pure ozone have been recorded at room temperature using the Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. Each spectrum covers the entire region from 1100 cm^{-1} to 2600 cm^{-1} and has a signal-to-noise ratio of at least 150:1. Initial analyses of these spectra in the 5 μm region have resulted in intensities for a number of lines in the $\nu_1 + \nu_3$, $2\nu_3$, and $\nu_1 + \nu_2 + \nu_3 - \nu_2$ bands, as well as self-broadened halfwidths in the $\nu_1 + \nu_3$ band. These preliminary results are in good agreement with previous measurements and calculations.

Address of Smith and Rinsland: Atmospheric Sciences Division, Mail Stop 401A, NASA Langley Research Center, Hampton, Virginia, 23665-5225.
Address of Malathy Devi and Benner: Physics Department, College of William and Mary, Williamsburg, Virginia, 23185.

RF8. (3:04)

THE ν_1 AND ν_3 BANDS OF $^{18}O^{16}O^{18}O$ AND $^{18}O^{18}O^{18}O$

J. M. FLAUD, C. CAMY-PEYRET, V. MALATHY DEVI, C. P. RINSLAND, AND M. A. H. SMITH

Using 0.005 cm^{-1} resolution Fourier transform spectra of ^{18}O-enriched ozone samples, it has been possible to perform an extensive analysis of the ν_1 and ν_3 bands of the two isotopic species $^{18}O^{16}O^{18}O$ and $^{18}O^{18}O^{18}O$. The experimental rotational energy levels of the (100) and (001) vibrational states of both species were then reproduced with the aid of an Hamiltonian taking explicitly into account the Coriolis interaction affecting the upper vibrational states. Precise vibrational energies and rotational constants were derived and used together with an appropriate expansion of the transformed transition moment operators of the ν_1 and ν_3 bands to generate a complete and reliable list of line positions and intensities for both the isotopic species $^{18}O^{16}O^{18}O$ and $^{18}O^{18}O^{18}O$.

Address of Flaud and Camy-Peyret: Laboratoire de Physique Moléculaire et d'Optique, Atmosphérique, Batiment 221, Campus d'Orsay, 91405 Orsay Cédex, France.
Address of Malathy Devi: Physics Department, College of William and Mary, Williamsburg, Virginia, 23185.
Address of Rinsland and Smith: NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665.

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LINE STRENGTHS AND PRESSURE BROADENING WIDTHS OF SOME SELECTED NO_2 LINES OF ATMOSPHERIC
IMPORTANCE USING DIODE LASER SPECTROSCOPY

A. FRIED AND R. L. SAMS

Measurements of NO_2 mixing ratios are very important in understanding the complex NO_x chemistry in both the lower and upper atmosphere. Many such measurements rely upon line strengths for transitions in the strongest band of NO_2 (v_3). We report here new measurements for a number of transitions which are of interest to atmospheric chemists. In order to adequately measure the strengths of some of the transitions whose spin splittings are not resolved, it was necessary to make new determinations of the spin-spin interaction terms. Several higher order terms were found to be significant.

The absorption measurements were carried out on known concentrations of NO_2 employing permeation standards (50-100 ppm) which have been extensively characterized by gravimetric and chemical titration techniques. This approach is different from traditional measurements where the number density of the absorbing species is derived from pressure measurements alone. Because of the well characterized low concentration source of NO_2, uncertainties in the number density due to decomposition and the presence of N_2O_4 are thus minimized. However, the low concentrations required the use of a long pass cell. A high resolution confocal interferometer and the technique of sweep integration were employed in these measurements. This both improved the signal to noise achieved and increased the accuracy of the line width measurements. Final results will be given and compared to unpublished results of Toth[1].

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[1]R. Toth private communication.

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Address of Fried and Sams: Center for Analytical Chemistry, Gas and Particulates Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RESEARCH ON THE IR ABSORPTION OF WATER DIMER

SHANXIONG SHEN, CAI PEIPEI, ZHANG HANSHENG, AND I-SHAN ZENG

Water vapor appears as a very important constituent of the earth's atmosphere. Its absorption is of greatest concern to system performance, but water vapor is difficult to control even in the laboratory, due to its attractive force toward surfaces. We used a 10 meters long White cell to measure the continuum IR absorption in the CO_2 laser band and ro-vibrational absorption as well. Results showned that the dimer binding energy was estimated at 5.5 Kcal. The concentration ratio, C_2/C_1 of the water monomer to dimer at room temperature and at its vapor pressure was obtained to be 1.2×10^{-3}

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Address: Department of Physics, East-China Normal University, Shanghai, 200062, People's Republic of China.

RF11.   (3:40)

NEW CALCULATIONS AND HIGH-TEMPERATURE MEASUREMENTS OF H_2O COLLISIONAL-BROADENING

J.M. HARTMANN, J. TAINE, J. BONAMY, B. LABANI, AND D. ROBERT

Comparisons between available room temperature infrared experimental H_2O line-widths and results of a recent semi-classical model[1] developped by the authors are presented. The latter, contrarily to those generally used up to now for H_2O collisional-broadening, provides a satisfactory treatment of close collisions through modellings of both trajectory modifications and short-range potential contributions; these improvements are demonstrated by the accurate results obtained for N_2-broadening of high rotational quantum number lines and for the broadenings associated to weakly (O_2) or non-polar (Ar) perturbers.

Accurate diode-laser measurements of H_2O infrared line-parameters in the 400-900 K temperature range are also presented. The measured self- and N_2-broadened widths of some high rotational quantum number lines show unusually slow decreasings with temperature. Detailled analysis of the data demonstrates the great influence of a "resonance overtaking" mechanism. The latter is well accounted for by our model and results from the modifications of both the velocities and perturber rovibrational populations distributions with temperature.

[1] B. Labani, J. Bonamy, D. Robert, J.M. Hartmann, and J. Taine, in press at J. Chem. Phys.

Address of Hartmann and Taine: Laboratoire d'Energétique Moléculaire et Macroscopique, Combustion, Ecole Centrale des Arts et Manufactures, Grande voie des vignes,92295 Chatenay-Malabry, France.
Address of Bonamy, Labani and Robert: Laboratoire de Physique moléculaire,Faculté des Sciences et Techniques, 25030 Besançon Cedex, France.

RG1.   (1:30)

SPECTROSCOPY OF SMALL, FUNDAMENTAL SPECIES IN THE MILLIMETER WAVE REGION USING A BROADBAND
SPECTROMETER

RANDY A. BOOKER, ERIC HERBST, FRANK C. DE LUCIA, JOHN G. BAKER, AND K. V. L. N. SASTRY

A summary of several projects that have been carried out recently using a broadband spectrometer system will be presented. Species to be discussed will include CH_3SH, CH_3COH, and CF_2CL_2. The data for these analyses were obtained using a broadband millimeter and submillimeter spectrometer that is based on traveling wave tube, harmonic generator, and cryogenic detector technology. The long continuous survey sweeps and fast computerized measurement of line frequencies that this system makes possible greatly facilitated the assignment and measurement of the spectra.

Address of Booker, Herbst, and De Lucia: Department of Physics, Duke University, Durham, NC 27706
Address of Baker: Schuster Laboratory, The University, Manchester, UK M139PL
Address of Sastry: Department of Physics, University of New Brunswick, Fredericton, NB, E3B5A3

RG2.   (1:47)

TIME RESOLVED ROTATIONAL ENERGY TRANSFER IN $^{13}CH_3F$

RODNEY L. McCORMICK, DAVID D. SKATRUD, AND FRANK C. DE LUCIA

Collisional energy transfer in optically pumped $^{13}CH_3F$ has been studied in a time resolved infrared/millimeter wave multiple resonance experiment. In this experiment a Q-switched CO_2 laser is used to rapidly populate J=5 in the v_3=1 excited vibrational state. The time evolution of the relaxation of the non-equilibrium population is then monitored via the millimeter wave probe. By appropriate selection of the rotational transition to be monitored, J changing, K changing, and v changing collisions can be studied with a minimum of theoretical deconvolution. A model has been developed to predict state-to-state population transfer rates. This model and the experimental results will be compared.

Address of McCormick and De Lucia: Department of Physics, Duke University, Durham, NC 27706
Address of Skatrud: U.S. Army Research Office, Research Triangle Park, NC 27709

RG3.   (2:04)

HYPERFINE CALCULATIONS USING AN UNCOUPLED REPRESENTATION

S. Young and S. Kukolich

An algorithm is presented for the determination of the effect of hyperfine coupling on rotational energy levels in a molecule containing an arbitrary number of coupling nuclei with arbitrary spin. The uncoupled representation is used, and matrix elements are given for the quadrupole, spin-rotation, spin-spin, and Stark interactions. The program can be expanded to include other multipole interactions if necessary. The case of three identical nuclei with spin of 1 is discussed. This program can also be used in choosing states for beam MASER spectroscopy. As an example, results of calculations are presented for two states of acetonitrile to determine which states will focus or defocus for various focussing voltages.

Address of Young: Department of Chemistry, University of South Alabama, Mobile, Alabama, 36688.
Address of Kukolich: Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

RG4.   (2:21)

MICROWAVE SPECTRA AND MOLECULAR STRUCTURE OF 1,1,2,2-TETRAFLUOROCYCLOPROPANE

R.N. BEAUCHAMP, N.C. CRAIG, AND C.W. GILLIES

The microwave spectrum of 1,1,2,2-tetrafluorocyclopropane was investigated in the region of 26.5 to 40.0 GHz. Assignments of the μ_c type R-branch transitions were made for the monodeuterated isotopic species and two lowest excited vibrational states of the dideuterated isotopic species, as well as the carbon-13 isotopic species:

$$^{13}CF_2CF_2CH_2, \quad CF_2CF_2{}^{13}CH_2, \quad CF_2CF_2{}^{13}CD_2.$$
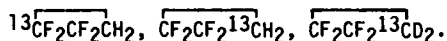
Transition frequencies were determined in R-band for the following previously assigned species[1]:

$$CF_2CF_2CH_2, \quad CF_2CF_2CD_2, \quad ^{13}CF_2CF_2CD_2,$$
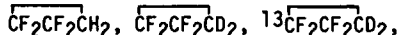
The data enable the calculation of a complete molecular structure in the d_0 and d_2 isotopic species framework. The structural parameters calculated in the d_0 frame are:

$r(C_1C_2) = 1.471(3)Å$ $r(C_1C_3) = 1.497(10)Å$ $r(C_1F) = 1.344(4)Å$

$r(C_3H) = 1.088(5)Å$ $\theta(FC_1F) = 109.9(4)°$ $\theta(HC_3H) = 118.0(4)°$

The structure obtained will be discussed in the context of experimental and theoretical studies of similar systems.

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[1] V.W. Laurie, W.M. Stigliani, Paper TF5, 30th Symposium on Molecular Spectroscopy, Columbus, Ohio (1975)

Address of Craig: Department of Chemistry, Oberlin College, Oberlin, Ohio 44074.
Address of Beauchamp and Gillies: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180.

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MICROWAVE SPECTRUM OF CIS-1,1,2,3-TETRAFLUOROCYCLOPROPANE

R.N. BEAUCHAMP, J. ZOZOM, AND C.W. GILLIES

The microwave spectrum of cis-1,1,2,3- tetrafluorocyclopropane has been investigated in the region of 26.5 to 40.0 GHz. A rigid-rotor fit of fifteen μ_c type R-branch transitions yields the rotational constants:

A = 3450.37(1) MHz   B = 2402.81(1) MHz   C = 2060.21(1) MHz

Transition frequencies were also determined for the two K_{-1} = 12 $\rightarrow$ 13 μ_c type Q-branch series from J = 13 to J = 28. Radio frequency - microwave double resonance techniques confirmed both the R and Q-branch assignments.

Address of Beauchamp, Zozom and Gillies: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180

MICROWAVE SPECTRUM OF 3-FLUORO-2-METHYLPROPENE

T. S. LITTLE, MENGZHANG ZHEN, H. QIU, AND J. R. DURIG

The microwave spectrum of 3-fluoro-2-methylpropene (methallyl fluoride) has been recorded in the region 18.0 to 39.0 GHz. The a-type R-branches have been observed and assigned in the ground and first two vibrationally excited states of the asymmetric torsion for both the low energy cis and high energy gauche conformers. Additionally, the c-type Q-branches for the gauche conformer and b-type Q-branches for the cis conformer have been assigned. The ground state rotational constants for the gauche conformer were found to have the following values: A = 7691.75 ± 0.02, B = 3900.77 ± 0.01 and C = 2876.85 ± 0.01 MHz whereas those for the cis are: A = 9035.14 ± 0.01, B = 3655.63 ± 0.01 and C = 2690.16 ± 0.01. From the Stark effect the dipole moment components were determined for the cis conformer to be $|\mu_a|$ = 1.65 ± 0.02, $|\mu_b|$ = 1.13 ± 0.01 and $|\mu_t|$ = 2.00 ± 0.01 D and those for the gauche conformer to be $|\mu_a|$ = 1.36 ± 0.03, $|\mu_b|$ = 0.26 ± 0.07, $|\mu_c|$ = 0.89 ± 0.07 and $|\mu_t|$ = 1.65 ± 0.01 D.

Address of Little, Durig, and Qiu: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.
Address of Zhen: The Institute of the Liming Chemical Industry, Luoyang, Henan Province, People's Republic of China.

MICROWAVE SPECTRA OF EIGHT ISOTOPIC SPECIES OF ETHYLPHOSPHINE

P. GRONER, R. D. JOHNSON, AND J. R. DURIG

The microwave spectra of eight isotopic species of ethylphosphine, $CH_3CH_2PH_2$, have been assigned for both the trans and gauche conformers. From these data improved molecular structure parameters have been obtained for both conformers. The changes in structural parameters with conformational change will be compared to those obtained for other similar molecules.

Address: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

RG8.

MICROWAVE SPECTRUM, STRUCTURE AND DIPOLE MOMENT OF TRIFLUOROMETHYL SILANE

G. ATTIA, P. GRONER, H. BURGER, AND J. R. DURIG

The microwave spectra of six isotopic species of trifluoromethyl silane, CF_3SiH_3, have been recorded from 18.5 to 39 GHz and R-branch a-type transitions have been assigned for the asymmetric tops. From these data the following r_0 structural parameters have been obtained: $r(Si-H) = 1.460 \pm 0.001$ Å, $r(C-Si) = 1.902 \pm 0.005$ Å, $r(C-F) = 1.360 \pm 0.002$ Å, $\angle CSiH = 107.17 \pm 0.01°$ and $\angle FCSi = 113.13 \pm 0.22°$. These results will be compared to some of the corresponding structural parameters for other trifluoromethyl-Group IVA hydrides.

Address of Attia, Groner, and Durig: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.
Address of Bürger: Anorganische Chemie, Universität-Gesamthochschule, 5600 Wuppertal, West Germany.

RG9.

MILLIMETER-WAVE OPTICAL DOUBLE RESONANCE SPECTRA OF NO_2:

IS N A GOOD QUANTUM NUMBER?

STEPHEN L. COY, KEVIN K. LEHMANN, AND FRANK C. DeLUCIA

The double resonance spectrum of NO_2 has been observed between three ground state millimeter wave transitions and the optical ^2B electronic state region. The probed ground state transitions were the N = 2, 4, and 10, K = 0-1 Q branches near 250 GHz, and the optical range scanned was 16800 cm^{-1} to 16950 cm^{-1}. The 10(0,10) – 10(1,9) F2 spectrum, when combined with results on the 9(1,9) – 10(0,10) F1 spectrum, establish violations of the $\Delta N = \Delta J$ selection rule, so that N is not a good quantum number in the upper state. The fraction of all possible symmetry-restricted basis states which contribute to a typical eigenstate, measured by Heller's F parameter, is similar for the three N values, but is greater for K = 1 than for K = 0. By identifying upper states in common, R lines from N = 2 and P lines from N = 4 have been identified.

Address of Coy: Dept. of Chemistry, Harvard University, Cambridge, Mass. 02138
Address of Lehmann: Dept. of Chemistry, Princeton University, Princeton, N.J. 08544
Address of DeLucia: Dept. of Physics, Duke University, Durham, N.C. 27706.

RG10.

MICROWAVE ANTICROSSING SPECTRUM OF AMMONIA

I. OZIER AND W.L. MEERTS

A microwave absorption anticrossing technique has been developed and used to observe in NH_3 an avoided crossing between the lower inversion level with (J=13, K=11) and the upper (14,14) level. It has been found that the zero-field separation between these levels is 678.60(10) MHz and that the distortion dipole moment is $1.247(76) \times 10^{-4}$ D.

Address of Ozier: Department of Physics, The University of British Columbia, Vancouver, B.C., V6T 2A6, Canada.
Address of Meerts: Fysisch Laboratorium, Katholieke Universiteit, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

RG11.   (4:28)

ACCIDENTAL 3-LEVEL DOUBLE RESONANCES IN THE 6-μm LASER-STARK SPECTRUM
OF $^{15}NH_3$

W. H. Weber

A series of accidental 3-level double resonances are observed in the
non-linear Stark spectrum of $^{15}NH_3$ obtained with a CO laser and an
intracavity cell. They are assigned as Doppler-free 2-photon absorptions
originating in the a(4,3) ground state level and terminating in the s2v2
+v4+1(6,4) level, with an exactly resonant s2v2(5,3) intermediate
state. These resonances occur in pairs, symmetrically located in the
Doppler wings on either side of the usual Lamb dips. They are comparable
in strength and width to the Lamb dips, but they have the opposite phase.
One of each pair is associated with co-propagating absorption, the other
being its counter-propagating partner. The co-propagating features are
particularly interesting, since they can be observed without a cavity and
their resonant field strengths do not depend on the laser frequency. They
also span a wide range in electric field, from 22 kV/cm to over 90 kV/cm,
and thus constitute an ideal series for establishing calibration standards
in field strength. The data are analyzed to determine term values and
Stark coefficients for the excited states.[1] The resulting fit gives an
rms error of ±290 kHz for 18 lines.

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[1] W. H. Weber, Chem. Phys. Letters **122**, 469 (1985).

Address of Weber: Physics Department, Research Staff, Ford Motor Company,
Dearborn, MI 48121.

RG12.   (4:40)

AMMONIA VIBRATIONAL BANDS BETWEEN 6500 CM^{-1} AND 12000 CM^{-1}:
ROTATIONAL ASSIGNMENT BASED ON MICROWAVE-OPTICAL DOUBLE RESONANCE

STEPHEN L. COY and KEVIN K. LEHMANN

The microwave-detected microwave-optical double resonance method has
been extended into the IR as far as 6500 cm⁻¹ by double Raman-shifting the
pulsed dye laser source. Ammonia bands now being analysed include the
region of 2 quanta of the N-H stretch at 6700 cm⁻¹, and other bands at 9200
cm⁻¹, 10200 cm⁻¹, 10800 cm⁻¹, and 11200 cm⁻¹. The analyses are based on
high-resolution absorption spectra at dry-ice and room temperature provided
by Don Ramsey and Bill Neal of the Herzberg Institute, and well as the
double resonance data. Current results will be discussed.

Address of Coy: Dept. of Chemistry, Harvard University,Cambridge, Mass.
02138
Address of Lehmann: Dept. of Chemistry, Princeton University, Princeton,
N.J. 08544

RG13.   (4:52)

Transition Dipole Moment Measurements for the ν_2 band of
NH_3 with Molecular Beam Laser Stark Spectroscopy

W.Q.Cai, T.E.Gough, X.J.Gu, N.R.Isenor and G.Scoles

Molecular beam laser Stark resonance spectroscopy using a supersonic He beam seeded with NH_3, a CO_2 laser source and optothermal bolometric detection has been applied to the determination of the transition dipole moment for the ν_2 band of NH_3.

Rabi oscillations in the ASR(110), $\Delta M=0$ and ASQ(222), $\Delta M=0$ transitions have been observed. The frequency (in terms of the laser field amplitude) of the oscillations was used to determine the transition dipole moment of the ν_2 band, yielding $\mu_{s,<-a}=0.261\pm0.006D$, in good agreement with other values recently reported in the literature. The rather large differences with the previously published values ($\sim30\%$) found recently in our laboratory for the ν_3 band of CH_3F are therefore confirmed. The hyperfine structure due to the electric quadrupole interaction of the nitrogen nucleus was clearly resolved. An absorption line width of 350 kHz and a eqQ value accurate to 0.5% were obtained.

Address: Center for Molecular Beam and Laser Chemistry, University of Waterloo, Waterloo Ontario Canada, N2L 3G1

RG14.   (5:04)

MICROWAVE FOURIER TRANSFORM SPECTROSCOPY
M. Oldani, B. Vogelsanger, and A. Bauder

It has been demonstrated that microwave Fourier transform (MWFT) spectroscopy is a sensitive method capable of detecting the rotational spectra of "nonpolar" molecules. We have applied MWFT spectroscopy to obtain vibronic ground state and ν_4 excited state rotational spectra of $^{12}CH_4$, $^{13}CH_4$, $^{13}CD_4$, and $^{28}SiH_4$. The tensorial centrifugal distortion constants of the ground vibrational state have been determined and the isotope effects compared to theoretical predictions. From the excited state spectra parameters of the ν_2/ν_4 dyad Hamiltonian have been determined.

In addition, we have observed the pure rotational spectra of allene-1,1-d_2 and allene-d_1. A set of rotational constants of allene-d_1 has been obtained for the first time. The resolving power of MWFT spectroscopy has been demonstrated by resolving the deuterium nuclear quadrupole hyperfine splittings of some rotational transitions of fluorobenzene-4-d_1.

Address: Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule Zürich, Universitätstrasse 22, CH-8092 ZURICH, Switzerland.

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(1:30)

DIRECT DETERMINATION OF LONG-RANGE INVERSE-POWER POTENTIAL COEFFICIENTS FROM VIBRATIONAL ENERGIES AND B_v VALUES

J. Shelley and R.J. Le Roy

At long range, the interaction potential for a diatomic molecule may be written as a sum of inverse power terms: $V(R) = D - \sum C_m/R_m$, where the contributing values of m are determined by the nature of the atomic dissociation products and the symmetry of the molecular electronic state. Values of the potential coefficients C_m (together with the dissociation limit D) may be determined from experiment in one of two ways: (i) RKR turning points may be fitted directly to the above expression,[1-3] or (ii) the energies of the levels closest to dissociation may be fitted to the limiting near-dissociation theory expression $G(v) = D - X_0(n)(v_D-v)^{2n/(n-2)}$ to yield values of D and of the leading inverse power coefficient.[1,4] However, parameters obtained from the former approach are very highly correlated, sometimes having sufficiently large statistical uncertainties to make their values virtually meaningless, while the latter approach is limited by the fact that it takes account of only the leading inverse-power potential term. The present paper describes a generalized near-dissociation theory approach which can take account of as many terms as desired in the long-range potential, and is based on fits to experimental vibrational energies and B_v values. The interparameter correlation associated with this new approach is much smaller than for the turning point fits, and the uncertainties in the input data (G(v)'s and B_v's rather than RKR turning points) may be properly estimated and taken into account.

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[3] S. Gerstenkorn, P. Luc and C. Amiot, J. Physique 46, 355 (1985).

[4] R.J. Le Roy and R.B. Bernstein, J. Chem. Phys., 52, 3869 (1970).

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

(1:47)

DETERMINING AN ATTRACTIVE DIATOM POTENTIAL WELL BY INVERSION OF BOUND-CONTINUUM EMISSION INTENSITIES

Robert J. Le Roy and William J. Keogh

In previous work,[1] an "RKR-like" inversion procedure for determining a repulsive diatom potential curve from the positions of the intensity extrema associated with continuum emission or absorption from a single vibrational level of a known bound state potential, was described and tested. The present paper presents and illustrates a complementary inversion procedure for determining the initial bound state curve associated with such a spectrum from the positions of these intensity extrema and knowledge of the repulsive final state curve. An application of the method to data[2] for the $^3\Sigma^+$ state of NaK also demonstrates the utility of this procedure for cases in which the experimental data are incomplete and the vibrational assignment of the initial level is not known.

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Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

RH3. (2:04)

VIBRATIONAL FREQUENCY SHIFTS OF SF_6 MOLECULES INSIDE AND ON THE SURFACE OF SOLID MATRICES OR MOLECULAR CLUSTERS.

D. Eichenauer and R.J. Le Roy

The ν_3 infrared band of SF_6 has been found to have different red shifts, relative to the free molecule frequency, depending on whether the chromophore is situated inside an Ar cluster, at the surface of an Ar cluster, or in an Ar matrix.[1-3] The present paper describes our work on a model for explaining these shifts in terms of the dependence of the Ar-SF_6 interaction potential on the vibrational stretching of the SF_6. The main contribution to this shift is found to arise from the vibrational dependence of the electrostatic field due to the oscillating dipole moment associated with the ν_3 mode of SF_6. The structures of SF_6-Ar_n clusters and of matrices containing SF_6 are investigated using the realistic, empirical rigid-body Ar-SF_6 pair potential of Pack et al.[4] The shifts of the SF_6 vibrational levels are then predicted by treating the influence of the surrounding atoms using this perturbation theory.

[1] T.E. Gough, D.G. Knight and G. Scoles, Chem. Phys. Lett., 97, 155 (1983).

[2] T.E. Gough, M. Mengel, P.A. Rowntree and G.Scoles, J. Chem. Phys., 83, 4958 (1985).

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Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

RH4. (2:21)

ANALYSIS OF METROPOLIS MONTE CARLO STUDIES OF A MODEL ICE Ih

P. W. Deutsch

Simulations performed upon a model Ice Ih lattice for input Kelvin temperatures of 20, 100, 200, and 260K are analysed statistically in the context of relevant experimental results. The results of x-ray diffraction experiments[1,2] coincide with derived simulation results within the limits of statistical uncertainties both in experiment and in simulation. Parallel simulations of elastic neutron diffraction are also performed and they are discussed in the context of elastic neutron diffraction data. For both the x-ray and neutron diffraction results[3,4], we focus on the virtual lack of temperature dependence between 100K and 200K in the simulations.

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[3] S. W. Peterson and H. A. Levy, Acta. Cryst. 10, 70-6 (1957).

[4] A. Zajac, J. Chem. Phys. 29, 1324-7 (1958).

Address of Author: The Pennsylvania State University at Beaver, Brodhead Road, Monaca, Pennsylvania 15061.

RH5. (2:38)

AB INITIO CALCULATION OF THE IR INTENSITIES OF STRETCHING VIBRATIONS OF COS AND CS_2

P. BOTSCHWINA AND P. SEBALD

The dependence of the electric dipole moment on the stretching vibrational coordinates for COS and CS_2 has been calculated by Meyer's Coupled Electron Pair Approximation, CEPA.[1] The dipole moment function obtained for COS is in good agreement with the preferred experimental function of Tanaka et al.[2] and the calculated IR intensities are in excellent agreement with experiment. The calculations for CS_2 strongly suggest that the previous experimental intensities of the ν_3 band are too low, probably due to saturation effects.

[1] W. Meyer, J. Chem. Phys. 58, 1017(1973).

[2] K. Tanaka, T. Tanaka, and I. Suzuki, J. Chem. Phys. 82, 2835 (1985).

Adress: Fachbereich Chemie der Universität Kaiserslautern, D-6750 Kaiserslautern, West Germany

RH6. (3:10)

ELECTRONIC SPECTRA OF ArH AND XeH

R.H. Lipson

To date there is no reference to any work carried out on XeH and only one band of ArH has been analyzed (1). Recently HeH and NeH have been studied (2) but none of the electronic states involved in the observed transitions for these molecules or for ArH have been assigned unambiguously.

New emission spectra of ArH and XeH will be presented. These molecules were produced using a supersonic jet discharge (3) and a Penning ionization cell (4). The observed Rydberg-Rydberg transitions exhibit large Λ doubling and in some cases, the large ℓ-uncoupling produces unusual rotational structure and branch intensities.

(1) J.W.C. Johns,J.Mol.Spect.36,488-510,(1970).
(2) W. Ketterle,H. Figger,and W. Walther,Phys.Rev.Letts.,55,2941-2944,(1985).
(3) A.T. Droege and P.C. Engleking,Chem.Phys.Letts.,96,316-318,(1983).
(4) D. Cossart,C. Cossart-Magos,G. Gandara,and J.M. Robbe,J.Mol.Spect.,109, 166-185,(1985).

Address: Herzberg Institute of Astrophysics,
         National Research Council of Canada,
         Ottawa,Ontario,K1A 0R6,Canada.

RH7.   (3:27)

RADIATIVE LIFETIME MEASUREMENTS FOR THE B $^3\Pi$ (0^+)
STATE OF CHLORINE MONOFLUORIDE

L.J. VAN DE BURGT and M.C. HEAVEN

Radiative lifetime measurements for the B $^3\Pi$ (0^+) state of ClF have been made for the first time. Pulsed laser excitation was used to excite a single ro-vibrational level ($v' = 5$, $J' = 16$) of the B state, and fluorescence decay curves were recorded for ClF pressures ranging from 0.001 to 0.2 torr. The resulting Stern-Volmer plot defined a radiative lifetime of $1.3\pm.3$ ms and a deactivation rate constant of 2.8×10^{-11} cm^3 molecule^{-1} s^{-1}. The observed radiative lifetime is in good agreement with the expected value of 1-3 ms, based on an extrapolation of data for the other interhalogens.[1]

The deactivation rate constant is most probably influenced by the effects of vibrational energy transfer. Relaxation red-shifts the fluorescence spectrum and this diminishes the efficiency with which the emission is detected by the photomultiplier. Therefore, the measured deactivation rate constant should be regarded as an upper limit for the electronic self quenching rate constant.

Further measurements are in progress, and a summary of the results will be presented.

(1). M.A.A. Clyne and E. Martinez, J.C.S. Faraday Trans. II **76**, 1275 (1980).

Address of van de Burgt and Heaven: Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616.

RH8.   (3:44)

LOW PRESSURE PHOTOACOUSTIC SPECTROSCOPY OF SMALL MOLECULES IN WHICH THE RF DISCHARGE IS USED AS SONIC SENSOR

D. KUMAR, P. L. CLANCY, L. KLASINC, R. V. NAUMAN, AND S. P. MCGLYNN

A new technique for low-pressure photoacoustic (PA) spectroscopy, in which a low-power radiofrequency (RF) discharge is used as a sensitive acoustic wave sensor, will be presented. The technique is a variation of the laser optogalvanic (LOG) method and is termed PARFLOG (photoacoustics using radiofrequency laser optogalvanic detection).

The method is contactless and applicable to the study of corrosive gases. The ability to prosecute low-pressure photoacoustic measurements at a reduced level of collisional perturbation makes possible the study of such intramolecular processes as level crossing, predissociation, field effects, etc. Results of PARFLOG studies of small molecules will be presented.

Address: Department of Chemistry, Louisiana State University,
         Baton Rouge, LA 70803

RH9.   (4:01)

ELECTRONIC SPECTROSCOPY OF THE CYANOGEN HALIDES

S. FELPS AND S. P. MCGLYNN

The electronic absorption spectra of the cyanogen halides, XCN with X=Cℓ, Br and I, are presented in the range 3100–1050Å. A comparison of the spectra of the cyanogen halides with those of the hydrogen and methyl halides shows that intravalence transitions are responsible for the differences in the electronic spectra of these species. An MO scheme that reliably predicts both the observed electronic spectroscopy and photochemistry is presented.

Address: Department of Chemistry, Louisiana State University, Baton
           Rouge, Louisiana, 70803

RH10.   (4:18)

PULSED LASER OPTOGALVANIC SPECTROSCOPY OF IODINE IN RF DISCHARGE

D. KUMAR, L. KLASINC, P. L. CLANCY, R. V. NAUMAN, AND S. P. MCGLYNN

Laser optogalvanic (LOG) spectra of iodine vapors (50–200 mTorr pressure) in an rf discharge ($\sim$30 MHz) have been studied by means of a pulsed, flash-lamp pumped, tunable dye laser. Signals were normalized on a pulse-by-pulse basis before averaging and the effective duty-cycle was forced towards unity in order to obtain smooth spectra even at low pulse-repetition rates.

Contrary to the usual arrangement, the pick-up coil was placed outside the rf excitation electrodes and excellent LOG signals were obtained when a transverse optical excitation was imposed in the region between the pick-up coil and the rf electrode. The LOG signal consists of two components: a fast component ($\sim$1μs) that is atomic in origin and is almost synchronous with the excitation laser pulse and a slow component (50–100μs) which is molecular in origin. The spectrum of the fast component, excited with 14900–17000cm^{-1} laser radiation, shows atomic (ionic as well as neutral) transitions originating from various excited states; that of the slow component, similarly excited, is the normal $\tilde{B}$ ← $\tilde{X}$ iodine molecular spectrum.

The nature and origin of the two distinct components in the LOG signal will be discussed and some spectroscopic analysis will be presented.

Address: Department of Chemistry, Louisiana State University
           Baton Rouge, LA 70803

(4:35)

RH11.

PULSED LASER OPTOGALVANIC SPECTROSCOPY OF BROMINE IN RF DISCHARGE

D. KUMAR, L. KLASINC, P. L. CLANCY, R. V. NAUMAN, AND S. P. MCGLYNN

Laser optogalvanic (LOG) spectra of bromine vapors (50-200 mTorr pressure) in an rf discharge ($\sim$30 MHz) have been studied by means of a pulsed, flash-lamp pumped, tunable dye laser. Signals were normalized on a pulse-by-pulse basis before averaging and the effective duty-cycle was forced towards unity in order to obtain smooth spectra even at low pulse-repetition rates.

Contrary to the usual arrangement, the pick-up coil was placed outside the rf excitation electrodes and excellent LOG signals were obtained when a transverse optical excitation was imposed in the region between the pick-up coil and the rf electrode. The LOG signal consists of two components: a fast component ($\sim$1µs) that is atomic in origin and is almost synchronous with the excitation laser pulse and a slow component (50-100µs) which is molecular in origin. The spectrum of the fast component, excited with 14900-17000cm^{-1} laser radiation, shows atomic (ionic as well as neutral) transitions originating from various excited states; that of the slow component, similarly excited, is the normal $\tilde{B} \leftarrow \tilde{X}$ bromine molecular spectrum.

The nature and origin of the two distinct components in the LOG signal will be discussed and some spectroscopic analysis will be presented.

Address: Department of Chemistry, Louisiana State University
Baton Rouge, LA 70803

(4:52)

RH12.

VACUUM ULTRAVIOLET LASER SPECTROSCOPY OF PERTURBED $^2\Delta$ STATES IN NO

J.W. HEPBURN AND D. HART

We have used tunable, coherent vacuum ultraviolet radiation to excite NO in a supersonic molecular beam. The excitation laser is tunable between 140 nm and 170 nm, and in this range the (9,0) to (0,0) bands of the $B'^2\Delta-X^2\Pi$ system can be excited.

By using pulsed excitation of single ro-vibronic states of NO in a molecular beam, it is possible to unambiguously determine the collision-free excited state lifetimes for a wide range of NO excited states.

We have studied Rydberg - Non-Rydberg interactions in the $B'^2\Delta$ state using this method, and as well have investigated the onset of predissociation in the $B'^2\Delta$ state.

Address: Centre for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

FA1.   (8:30)

ROTATIONAL SPECTRA OF MOLECULAR IONS USING TUNABLE DIODE LASER

DI-JIA LIU, WING-CHEUNG HO, and TAKESHI OKA

We report the first application of tunable infrared diode lasers for studies of the pure rotational spectra of molecular ions with large rotational constants. High J rotational transitions of cations ArH^+, NeH^+, HeH^+, OH^+, H_2O^+ and anion OH^- have been observed in the 22-27 μm region in AC glow discharge. The numbers of the molecular ions in such high rotational levels are small, but the spectral lines were observed with good signal to noise ratios because of the large permenent dipole moments of these ions.

The frequencies of the observed spectra determined or improved the centifugal distortion constants for some ions.

OH^- is the first negative ion whose rotational spectrum was directly observed. During the study of OH^- formation chemistry, we found that the concentration of OH^- could be greatly enhanced by using metal coated discharge tubes. Under the best conditions in a Pt-coated discharge tube, the OH^- concentration was estimated to 10^{10} cm^{-3}. Our observation of the dependance of OH^- concentration on discharge condition will be presented.

Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637.

FA2.   (8:47)

ROTATIONAL SPECTROSCOPY OF MOLECULAR IONS WITH TUNABLE FAR INFRARED LASERS

K.B. LAUGHLIN, G.A. BLAKE, R. COHEN, AND R.J. SAYKALLY

Tunable far-infrared radiation, produced by mixing an optically pumped far-infrared laser and a microwave oscillator in a Schottky diode, has been used to measure rotational spectra of several molecular ions. The ions were produced in a magnetically confined extended negative glow discharge. Spectra of HCO^+, HNN^+, ArH^+, and deuterated analogs will be presented. Progress on other systems will be reported.

Address of Laughlin, Blake, Cohen, and Saykally: Department of Chemistry, University of California, Berkeley, CA 94720.

FA3.   (8:59)

MEASUREMENT OF THE VIBRATION-ROTATION SPECTRUM OF THE HYDROXIDE ANION (OH⁻) BY VELOCITY MODULATION LASER SPECTROSCOPY

N.H. ROSENBAUM, J.C. OWRUTSKY, L.M. TACK, and R.J. SAYKALLY

Guided by the ab initio predictions for the OH^- fundamental made by Lee and Schaefer (1) and by Werner, Rosmus, and Reinsch (2) along with the laser photodetachment results of Schulz et al. (3), we measured the ν_{1+0} band of $^{16}OH^-$ and $^{18}OH^-$ by velocity modulation spectroscopy with a color center laser (4). The OH^- concentration was found to be maximized in a $Ar/H_2/O_2$ or $Ar/H_2/H_2O$ discharge where the addition of argon both rotationally heats the OH^- and increases its overall concentration. The OH^- signal was also found to be dramatically dependent on the presence of metal sputtered on the discharge cell wall. The $^{16}OH^-$ and $^{18}OH^-$ bands were analyzed separately with a least squares analysis yielding the equilibrium bond length and vibration-rotation constants through sextic distortion terms. Using the band origins of the two isotopomers, the harmonic vibrational frequencies and first order anharmonicities were calculated.

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2. H.-J. Werner, P. Rosmus, and E.-A. Reinsch, J. Chem. Phys. 79, 905 (1983).
3. P.A. Schulz, R.D. Mead, P.L. Jones, and W.C. Lineberger, J. Chem. Phys. 77, 1153 (1982).
4. N.H. Rosenbaum, J.C. Owrutsky, L.M. Tack, and R.J. Saykally, J. Chem. Phys. (accepted).

Address of Rosenbaum, Owrutsky, Tack, and Saykally: Department of Chemistry, University of California, Berkeley, CA 94720.

FA4.   (9:11)

INFRARED SPECTRUM OF THE FUNDAMENTAL VIBRATION-ROTATION BAND OF OD⁻

B.D.REHFUSS, M.W.CROFTON and T.OKA

Following the spectroscopic results on OH⁻,[1,2] the fundamental $v=1\leftarrow0$ vibration-rotation band of OD⁻ has been observed using the tunable infrared radiation from a difference frequency laser system and the velocity modulation technique for detection. OD⁻ was produced in an AC discharge with a mixture of $D_2:O_2$ in a 1:3 ratio. The spectrum has led to the following molecular constants: $\nu_0=2625.332(3)cm^{-1}$, $B_0= 9.98459(21)$, $B_1= 9.68615(19)$, $D_0= 5.549(15)\times10^{-4}$, $D_1= 5.470(12)\times10^{-4}$. A remarkable similarity between molecular constants of OD⁻ and OD has been noticed and utilized to obtain the following equilibrium constants: $\omega_e=2723.4(10)cm^{-1}$, $\omega_e x_e=49.65(50)$, $\omega_e y_e=0.38(15)$, $B_e=10.13599(30)$, $\alpha_e=0.3043(5)$, $\gamma_e=0.292(20)\times10^{-2}$, $D_e=5.588(18)\times10^{-4}$, $\beta_e=0.079(19)\times10^{-4}$. These vibration-rotation constants were used to determine the equilibrium bond length $r_e=0.96425(8)Å$ and the quadratic, cubic and quartic force constants: $F_2=7.82mdyne/Å$, $F_3=-57.0mdyne/Å$, $F_4=364mdyne/Å^3$. The similarity between OD⁻ and OD will be discussed in light of the obtained results.

[1] J.C.Owrutsky, N.H.Rosenbaum, L.M.Tack and R.J.Saykally, JCP 83, 5338(1985).
[2] D.J.Liu and T.Oka, JCP 84, 1312(1986).

Address of Authors: Department of Chemistry and Astronomy and Astrophysics, The University
                      of Chicago, Chicago, Illinois 60637

FA5.   (9:28)

DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF MOLECULAR IONS

T.Nakanaga and T.Amano

A hollow cathode discharge cell has proven to be an excellent source of positive ions. In the past few years, we have attained a significant improvement in sensitivity of the system which enables us to search for weaker lines of more complicated ions. In this talk, we will present our recent results on three symmetric top ions of astrophysical interest, NH_3D^+, CH_3CNH^+, and SH_3^+, detected in absorption in a modulated discharge through the mixtures of NH_3 and D_2, CH_3CN and H_2, and H_2S and H_2, respectively.

This is the first high-resolution spectroscopic detection of CH_3CNH^+ and SH_3^+. Both the ν_1 band of $CH_3CNH^+(\nu_0=3527.288$ cm^{-1}) and the ν_3 band of $SH_3^+(\nu_0=2525.78$ cm^{-1}) exhibit a clear sign of perturbations. In SH_3^+, the perturbation is more conspicuous, and an extra band yet to be identified is also observed. The rotational constants for the ground state have been determined for both SH_3^+ and CH_3CNH^+ through a least squares fit by using the combination differences. The lines of SH_3^+ show no sign of the inversion doubling, and the preliminary molecular constants obtained agree well with ab initio predictions. The rotational transition frequencies have been calculated to assist in future search for these ions in interstellar space.

NH_3D^+ possesses a permanent dipole moment of about 0.26 D, and it will be possible to detect the rotational transitions in the millimeter and sub-millimeter-wave region in interstellar space and in the laboratory. Our analysis of the ν_4 fundamental band($\nu_0=3341.0764$ cm^{-1}) provides a prediction of the rotational transition frequencies.

Address of Nakanaga and Amano: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

150

FA6.

PLASMA DIAGNOSIS USING INFARED SPECTROSCOPY: ANOMALOUSLY HIGH POPULATION OF THE v=3 LEVEL AND DOUBLING OF ArH$^+$ SPECTRAL LINES DUE TO DOPPLER SHIFT IN AN AC DISCHARGE

DI-JIA LIU, WING-CHEUNG HO AND TAKESHI OKA

Among the molecular ions so far studied, ArH$^+$ is special in that its abundance in discharges is very high and that highly excited vibration-rotation states are populated[1,2]. We have observed two anomalous effects in high J(R(20)-R(24)) rotational spectrum of ArH$^+$ for five vibrational states (v=0-4).

(A) The rotational spectral line corresponding to v=3 vibrational state is stronger than the lines in other vibrational states under certain discharge conditions with high Ar pressure, while spectral lines for other vibrational states are approximately thermal. Our observation indicates that ArH$^+$ is initially produced in the v=3 state after the ion-molecule reaction and that its vibrational relaxation is slow.

(B) We have observed splitting of spectral lines due to AC Doppler effect which gives directly the ion velocity and then the ion mobility in the discharge[3].

Observation and analysis of these results will be presented.

(1) J. W. Brault and S. P. Davis, Physica Scripta 25, 268 (1982)
(2) J. W. C. Johns, J. Mol. Spectrosc. 106,124 (1984)
(3) N. N. Haese, F. S. Pan and T. Oka, Phys. Rev. Lett. 50, 1575 (1983)

Address of authors: Department of Chemistry and Astronomy & Astrophysics, the University of Chicago, Chicago, IL 60637.

FA7.

AN ATTEMPT TO MEASURE ELECTRIC FIELD IN A D.C. GLOW DISCHARGE USING SUB-DOPPLER INFRARED SPECTRUM OF CH3F

FU-SHIH PAN, W.A. KREINER AND T. OKA

Plasma diagnostics using laser spectrometers has been successful in measuring ion mobility[1], ion density distribution[2] and high electric field in the cathode region[3]. We have attempted to measure the electric field in situ in the positive column of D.C. glow discharges by observing first order Stark splitting of CH3F Lamb dips using CO2-Microwave side band spectrometer. The strong R(4,3) transition gave clear Lamb-dip signals for the pressure range from 10 to 60 mTorr (approximately) in discharges and was used as the monitor. Varying discharge conditions and two air cooled discharge cells were used. No Stark splitting was observed even with discharge voltage of up to 24kV.

1.N.N.Haese,F.Pan and T.Oka, Phys. Rev. Letter,50,1575(1983).
2.F.Pan and T.Oka, to be published (1986).
3.C.A.Moore, G.P.Davis and R.A.Gottscho, Phys. Rev. Letter,52;
   538 (1984).

Department of Chemistry and Astronomy & Astrophysics, the University of Chicago, Chicago, IL.60637.

FA8. (10:37)

PRECISE MEASUREMENT OF FINE STRUCTURE INTERVALS IN ATOMIC IONS BY LASER MAGNETIC RESONANCE SPECTROSCOPY: N^+ AND C^+

A.L. COOKSY, D.C. HOVDE, G.A. BLAKE, AND R.J. SAYKALLY

Direct observation of the $J=2 \leftarrow 1$ fine structure transition in ^3P N^+ and the $J=3/2 \leftarrow 1/2$ transition in ^2P C^+ by far-infrared laser magnetic resonance spectroscopy has led to the precise evaluation of these fine structure splittings and corresponding g_J-factors and hyperfine parameters. These values are expected to facilitate the observation and analysis of these transitions in the interstellar medium.

Address of Cooksy, Hovde, Blake, and Saykally: Department of Chemistry, University of California, Berkeley, CA 94720

FA9. (10:49)

INFRARED SPECTRUM OF THE RENNER-TELLER ACTIVE ν_2 BAND of $X^2\Pi_g CO_2^+$ *

T. J. SEARS

The ν_2, bending, fundamental band of CO_2^+ has been detected by diode laser absorption spectroscopy at wavelengths between 17.5 μm and 22.2 μm. The combined effects of vibronic and spin orbit coupling split the spectrum into several well separated component bands and information on all of the vibronic components associated with $v_2 = 0$ and 1 has been obtained. Analysis of the spectra has yielded precise estimates of the rotational, Λ-doubling and spin uncoupling parameters while the vibronic splittings give information on the spin orbit coupling and the vibronic potential functions.

Address of Sears: Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973.

FA10. (11:06)

OBSERVATION OF THE $v_2 = 2^+ \leftarrow 1^-$ HOT 'AND OF H_3O^+ *

T. J. SEARS, P. B. DAVIES, AND S. A. JOHNSON

The $v_2 = 2^+ \leftarrow 1^-$ vibrational spectrum in H_3O^+ has been detected at wavelengths between 15 μm and 22 μm by diode laser absorption spectroscopy. The ion was generated in a glow discharge in a mixture of hydrogen and oxygen. The successful assignment of the spectrum depended to a large extent on the availability of reliable theoretical estimates of the band origin and structure since even the strongest lines are comparatively weak and lie in a crowded part of the oxonium ion spectrum. The band origin was found to be at 521.4 cm^{-1} which compares well with the most recent prediction[1] based on extrapolation from previously observed lower lying levels. The 2^+ level, by analogy with ammonia, is expected to be perturbed by the $v_4 = 1$ level and we find that it is not possible to fit the observed rotational structure to within the expected precision using the standard symmetric top formulae. However, without independent information regarding the $v_4 = 1$ level, detailed analyses of the perturbations are not possible.

[1] T. J. Sears, P. R. Bunker, P. B. Davies, S. A. Johnson and V. Špirko, J. Chem. Phys. **83**, 2676 (1985).

Address of Sears: Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973.

Address of Davies and Johnson: Physical Chemistry Department, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, England.

FA11.

AN AB INITIO CALCULATION OF THE EQUILIBRIUM GEOMETRY AND BARRIER

HEIGHT TO INVERSION OF H_3O^+ AND THE PROTON AFFINITY OF H_2O

P. BOTSCHWINA

The equilibrium geometry and barrier height to inversion

of H_3O^+ have been calculated by CEPA using a large basis set

of 103 contracted Gaussian type orbitals. The results are:

$r_e = 0.9745$ Å, $\theta_e = 16.94°$, and BH (barrier height) $= 679$ cm^{-1}.

These results are in very good agreement with the values deduced

from laser IR spectroscopy by Sears et al.[1] The proton affinity

of H_2O at zero temperature is calculated to be 687 kJ mol^{-1} and

lies within the error bars of the experimental value of Ng et

al.[2]

[1] T. J. Sears, P. R. Bunker, P. B. Davies, S. A. Johnson, and

V. Spirko, J. Chem. Phys. **83**, 2676(1985).

[2] C. Y. Ng, D. J. Trevor, P. W. Tiedemann, S. T. Ceyer, P. L.

Kronebusch, B. H. Mahan, and Y. T. Lee, J. Chem. Phys. **67**, 4235

(1977).

Adress: Fachbereich Chemie der Universität Kaiserslautern, D-6750

Kaiserslautern, West Germany

FA12.

MEASUREMENT OF THE ν_4 BAND OF H_3O^+ BY VELOCITY MODULATION DIODE LASER SPECTROSCOPY

M. GRUEBELE, M. POLAK, AND R.J. SAYKALLY

Diode laser spectroscopy has been used with velocity modulation detection to measure ~300 transitions of H_3O^+ in the range from 1400-1850 cm^{-1}. A preliminary analysis indicates that the $\nu_4 \leftrightarrow$ and $\nu_4 \rightarrow\leftarrow$ bandheads lie at higher frequency than predicted theoretically (1). The line density in some regions of the spectrum greatly exceeds that expected from a single perpendicular inversion band. Progress in the analysis will be reported.

1. P.R. Bunker, W.P. Kraemer, V. Spirko, J. Mol. Spec. **101**, 180 (1983).

Address of Gruebele, Polak, and Saykally: Department of Chemistry, University of California, Berkeley, CA 94720.

FA13.

AB INITIO CALCULATION OF POTENTIAL ENERGY SURFACES AND SPEC-
TROSCOPIC PROPERTIES OF H_2S AND H_3S^+

P. BOTSCHWINA, A. ZILCH, H.-J. WERNER, P. ROSMUS AND E.-A. REINSCH

The potential energy surface of H_2S has been computed by CEPA using a basis set of 66 contracted Gaussian type orbitals. Vibrational term energies and wave functions are calculated variationally and the fundamental vibrational frequencies (in cm^{-1}) are $\nu_1 = 2610(2614)$, $\nu_2 = 1202(1183)$, and $\nu_3 = 2620(2628)$, where experimental values are given in parentheses. The equilibrium geometry of H_3S^+ is $r_e = 1.350$ Å and $\theta_e = 32.21°$ and the barrier height to inversion amounts to 11 136 cm^{-1}. Various spectroscopic properties of the sulfonium ion are predicted.

Adress of Botschwina: FB Chemie der Univers. Kaiserslautern,

D-6750 Kaiserslautern, West Germany

Adress of Zilch, Werner, Rosmus, and Reinsch: FB Chemie der Univ.

Frankfurt, D-6000 Frankfurt, West Germany

FA14.

MEASUREMENT OF ROTATIONAL SPECTRA, ROTATIONAL G-FACTORS, AND THE EQUILIBRIUM BOND LENGTH FOR ArH^+ BY TUNABLE FAR-INFRARED LASER SPECTROSCOPY

K.B. LAUGHLIN, G.A. BLAKE, R. COHEN, AND R.J. SAYKALLY

Rotational spectra of ArH^+ and ArD^+ were measured in a magnetically confined plasma with a tunable far-infrared laser. By separating the $\Delta M_J = \pm 1$ components with a quarter wave plate, the rotational g-factors were determined. Combining this data with that available from microwave[1] and infrared spectroscopy[2,3] we can evaluate the Born-Oppenheimer equilibrium internuclear separation.

1. W.C. Bowman, G.M. Plummer, E. Herbst, and F.C. DeLucia, J. Chem. Phys. 79, 2093 (1983).
2. J.W. Brault and S.P. Davis, Phys. Scrip. 25, 268 (1982).
3. J.W.C. Johns, J. Mol. Spec., 106, 124 (1984).

Address of Laughlin, Blake, Cohen and Saykally: Department of Chemistry, University of California, Berkeley, CA 94720

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FB1.

TIME-RESOLVED STUDIES OF INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION IN S_1 BENZENE

DAVID B. MOSS AND CHARLES S. PARMENTER

Chemical timing (oxygen quenching) has been used to obtain time-resolved dispersed fluorescence spectra from single vibronic levels in S_1 ($^1B_{2u}$) benzene. The spectra reveal a dynamic intramolecular vibrational redistribution (IVR) on a picosecond time scale. The results are comparable to those previously obtained for p-difluorobenzene[1] and p-fluorotoluene.[2] The measured redistribution rates are two orders of magnitude faster than the electronic state decay referred to as "channel three".[3] The redistribution lifetimes are comparable to those inferred from linewidths of single rovibronic transitions, as observed in high resolution electronic absorption spectra.[4] This agreement suggests that IVR is the cause of the broad absorption linewidths. Implications of these results with regard to the mechanism for channel three decay will also be discussed.

[1] K.W. Holtzclaw and C.S. Parmenter, J. Chem. Phys., **84**, 1099 (1986).
[2] D.A. Dolson, C.S. Parmenter, and B.M. Stone, Chem. Phys. Lett., **81**, 360 (1981).
[3] J.H. Callomon, Faraday Disc. Chem. Soc. **75**, 417 (1983).
[4] J.H. Callomon, J.E. Parkin, and R. Lopez-Delgado, Chem. Phys. Lett. **13**, 125 (1972).

Address of Authors: Department of Chemistry, Indiana University, Bloomington, IN 47405

FB2.

IVR IN S_1 p-FLUOROTOLUENE

R.J. LONGFELLOW, D.B. MOSS, C.S. PARMENTER AND B.M. STONE

The chemical timing method[1] for obtaining picosecond time resolved fluorescence spectra was used to measure intramolecular vibrational redistribution (IVR) parameters in S_1 p-fluorotoluene (pFT). These parameters were determined for several levels and compared to those for the corresponding levels in p-difluorobenzene (pDFB)[1] pFT and pDFB have nearly identical $S_1 \leftarrow S_0$ absorption spectra and aromatic ring vibrational frequencies but were found to have significantly different IVR parameters. This observation is consistent with previous qualitative results regarding vibrational level mixing in pFT and pDFB[2]. Possible causes for these differences include the reduction of molecular symmetry and the coupling of torsional to vibrational motions will be discussed.

[1] K.W. Holtzclaw and C.S. Parmenter, J. Chem. Phys., **84**, 1099 (1986).
[2] C.S. Parmenter and B.M. Stone, J. Chem. Phys., (in press).

Address of Authors: Department of Chemistry, Indiana University, Bloomington, IN 47405

FB3. (9:04)

INFRARED SPECTROSCOPY OF SMALL MOLECULES ADSORBED ON SODIUM CHLORIDE SURFACES

H.H. RICHARDSON, J.A. EDLING AND G.E. EWING

The physisorption of small molecules (CO, N_2, CH_4) on sodium chloride surfaces is probed with Fourier Transformed Infrared Spectroscopy. Information concerning adsorption and desorption kinetics, molecular orientation on the surface and heat of adsorption as a function of surface coverage can be elucidated with this powerful too. Spectroscopic results will be interpreted in terms of theories of physisorption on alkali halide surfaces.

Address of Authors: Department of Chemistry, Indiana University, Bloomington, IN 47405

FB4. (9:21)

TRANSFER AND STORAGE OF VIBRATIONAL ENERGY IN LIQUIDS: COLLISIONAL UP-PUMPING OF CARBON MONOXIDE IN LIQUID ARGON

DEON S. ANEX AND GEORGE E. EWING

Isotopically enriched carbon monoxide (88% $^{13}C^{16}O$, 12% $^{13}C^{18}O$) dissolved in liquid argon was optically pumped to the $\nu = 1$ level by a CW CO laser. This energy was then redistributed by collisional up-pumping to higher vibrational levels. Fluorescence from vibrational levels up to $\nu = 20$ of the heavier isotope was observed from the steady-state distribution. The features of the population distribution are discussed in terms of the strength of optical pumping, carbon monoxide concentration, translational temperature, and the pertinent rate constants for energy transfer. For some conditions the populations of the vibrational levels are inverted. The potential for these solutions to store vibrational energy is discussed.

Address of Authors: Department of Chemistry, Indiana University, Bloomington, IN 47405

FB5. (9:38)

COLLISIONAL RELEASE OF Br_2

J. E. SMEDLEY, H. K. HAUGEN, AND S. R. LEONE[*]

The process of collisional dissociation of highly vibrationally excited B-state Br_2 is investigated in this study. A pulsed laser excites specific rovibrational levels which lie 1-5 kT below the B-state dissociation limit. Collisions "pump" the molecules up to form $Br(^2P_{3/2}) + Br^*(^2P_{1/2})$ products, which are detected by IR fluorescence and/or transient absorption-gain probing with an F-center laser at 2.7 µm.

The yield of Br^* is measured as a function of the energy of the prepared state below the dissociation limit, for both Br_2 and rare gas collision partners. Quenching by predissociation, both collision-induced and collision free, is a competing process. These rates are also presented.

Ground state Br_2 is an especially effective collisional release partner. The implications of this result with respect to possible mechanisms for collisional release are discussed.

[*]Staff member, Quantum Physics Division, National Bureau of Standards.

Address of Smedley and Leone: Joint Institute for Laboratory Astrophysics and Department of Chemistry, Boulder, Colorado 80309-0440.
Address of Haugen: Department of Physics, University of Toronto, Toronto, Ontario, Canada, M5S 1A7.

FB6. (9:50)

EVOLUTION OF N_2 EXCITED STATE VIBRATIONAL LEVEL POPULATIONS IN A PULSED ELECTRIC DISCHARGE

J. S. Morrill and W. M. Benesch

Experiments have been conducted to elucidate the processes governing the distribution of population among the molecular nitrogen triplet state vibrational levels under circumstances where molecular collisions are important. The conditions of the experiments are maintained so as to permit the application of the results to an understanding of similar processes in low altitude aurora. Nitrogen gas, at pressures of 0.03 to 3.0 Torr, is excited by means of a pulsed electric discharge which, typically, is supplied with pulses of 12,000 volts and 1,000 amperes and durations of 4 μsec in a large volume glass container. The radiation issuing from the discharge tube is analyzed by means of time-resolved spectroscopy with particular attention being given to the nitrogen First Positive System, $B^3\Pi_g \rightarrow A^3\Sigma_u^+$.

Dramatic changes have been noted in the relative band intensities of these spectra subject to the influence of the variation of the experimental conditions. In particular, the distribution of population among vibrational levels of the $B^3\Pi_g$ state evolves with time both during and after the exciting electric pulse with the trend strongly correlated with the number of collisions, independent of pressure. Further, emission from these excited vibrational levels continues at much higher rates than those commensurate with their radiative lifetimes. Both of these observations constitute evidence of the intersystem collisional transfer of excitation.

Additional studies show that the initial $B^3\Pi_g$ (upper state) vibrational population distributions produced during the excitation pulse vary with discharge pulse frequency. An increase of pulse frequency from a low to a high rate gives rise to a trend in the spectrum from one similar to an auroral distribution to one characteristic of a DC discharge. Analysis of these initial populations gives strong indication that excitation is occurring from an elevated vibrational distribution within the ground state. Results imply that this ground state distribution is quasi-Boltzmann with vibrational temperatures of up to 2500°K.

Address: Institute for Molecular Physics, University of Maryland, College Park, MD 20742

FB7. (10:20)

HIGH-TEMPERATURE QUENCHING OF CH ($A^2\Delta$, v'=0)

NANCY L. GARLAND AND DAVID R. CROSLEY

Quenching rate constants for the $A^2\Delta$ v'=0 state of CH have been obtained in a laser pyrolysis/laser fluorescence (LP/LF) system for a variety of collision partners. In the LP/LF cell, a CO_2 laser pulse irradiates a gas mixture of SF_6, CF_4, and CH_4 and quencher, rapidly heating the system to 1300 K. Abstraction of H atoms from CH_4 by F atoms (produced by the thermal decomposition of SF_6) generates CH radicals. Ground state CH radicals are excited to the $A^2\Delta$ state by a pulsed dye laser and the fluorescence lifetime is measured as a function of quencher pressure.

The cross sections (A^2) at 1300 K are:

CO	O_2	H_2	D_2	N_2	N_2O	CO_2	NH_3
8.5 ± 1.0	2.8 ± 0.4	3.6 ± 0.4	3.8 ± 0.4	1.3 ± 0.2	5.5 ± 0.7	2.2 ± 0.3	22.5 ± 3.0

These cross sections will be compared with those measured in this laboratory for NH and OH at high temperature (>1000K) and also with results from room temperature CH quenching experiments which are in progress.

Address of Authors: Molecular Physics Department, SRI International, Menlo Park, CA 94025

SLOW INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION (IVR) IN ISOLATED BENZENE MOLECULES

DONALD A. CHERNOFF, JAMES D. MYERS, AND J. GARY PRUETT

We report small homogeneous widths of high overtones of mode 1 (C-C ring breathing) in benzene and benzene-d_6, in contrast with much larger widths of C-H stretch overtones at similar energies. From the uncertainty principle, these widths provide an upper bound to the potential rate of IVR.

We used a tunable, nsec UV laser to excite benzene molecules seeded in a supersonic free jet to the $6^1 1^2$ vibrational level in the S_1 electronic state. We recorded emission spectra including transitions terminating at various levels up to ca. 10,000 cm^{-1} in the S_0 state. With the same upper state, any changes in transition linewidth would be characteristic of the lower state.

Our emission spectra consist of several hundred sharp vibrational bands and a congested background which breaks into many additional bands at higher resolution. Our major finding is that the sharp structure persists throughout the spectrum. Most of these bands can be assigned readily; in particular, we have located members of the $6_0^1 1_n^2$ progression. A comparison of the band shapes in this progression indicates little or no change in width. Considering our limiting spectral resolution of 13.5 cm^{-1}, we estimate that the homogeneous linewidths of the highest levels we observe are probably less than 5 cm^{-1} for both benzene and benzene-d_6.

This result is significantly different from that found by Reddy and co-workers for the C-H and C-D stretching overtones (homogeneous widths of 23 cm^{-1} for $3\nu_{CH}$ at 8786 cm^{-1} in benzene and 53 cm^{-1} for $4\nu_{CD}$ at 8734 cm^{-1} in benzene-d_6).[1] Clearly, the couplings of the C-C ring breathing mode to other modes are much different.

[1] K.V. Reddy, D.F. Heller and M.J. Berry, J. Chem. Phys. **76**, 2814(1982).

Address of Chernoff and Pruett: Corporate Research Center, The Standard Oil Company (Ohio), 4440 Warrensville Center Road, Warrensville Heights, Ohio 44128.
Address of Myers: Dept. of Chemistry, U. of Calif., Berkeley, CA 94720.

PHOTOELECTRON SPECTROSCOPY OF $(H_2O)_n^-$

J. V. Coe, D. R. Worsnop, and K. H. Bowen

It has often been suggested that gas-phase $(H_2O)_n^-$ clusters ought to exist, and that some might be counterparts to solvated (hydrated) electrons. Recently, these entities were observed in the gas-phase by Haberland et al. Here, we report the first spectroscopic study of the gas-phase negative cluster ions, $(H_2O)_n^-$. Using 2.409 eV photons, we have recorded the negative ion photoelectron (photodetachment) spectra of $(H_2O)_{n=11-15,19}^-$. These spectra consist of single broadened peaks each of which are shifted to successively higher electron binding energies with increasing cluster size. The implications of these results regarding the nature of $(H_2O)_n^-$ will be discussed.

Address of Coe and Bowen: Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218.
Address of Worsnop: Aerodyne Corporation, Billerica, MA 01821-3976.

FB10.   (11:11)

NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF P_2^-

J. T. Snodgrass, J. V. Coe, C. B. Freidhoff, K. M. McHugh, and K. H. Bowen

We have recorded the photoelectron spectrum of P_2^- using a cold-cathode discharge ion source and a negative ion photoelectron spectrometer. We obtain a highly structured spectrum from which we have determined the electron affinity of P_2 to be 0.589 ± 0.025 eV. Using this value for the electron affinity of P_2 along with the electron affinity of P and the bond dissociation energy of P_2 in a thermochemical cycle, the bond dissociation energy of P_2^- is calculated to be 4.88 ± 0.06 eV. A Franck-Condon analysis of the spectrum was used to confirm peak assignments and to determine spectroscopic parameters for P_2^-. We find $\omega_e''(P_2^-)$ = 640 ± 50 cm^{-1} and $B_e''(P_2^-)$ = 0.2776 ± 0.0028 cm^{-1} which leads to $R_e''(P_2^-)$ = 1.979 ± 0.010 Å. The positive electron affinity which we have measured for P_2 compared to the non-positive electron affinity of N_2 emphasizes the often noted electronic differences between phosphorus and nitrogen.

Address of Investigators: Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218.

FC1.   (8:30)

CALCULATION OF THE COMPLETE SET OF OBSERVABLES FOR ELASTIC LIGHT SCATTERING BY
RAMDOMLY ORIENTED MACROMOLECULES

W. M. McClain, and W. A. Ghoul
     We calculate the Perrin scattering matrix, which links the four Stokes parameters
of light scattered by a dilute solution of macromolecules to the Stokes parameters of
the incident light. Our algorithm involves the analytic average over all orientations
of the macromolecule, which may be of arbitrary size and shape. We show that certain
Perrin elements, which we previously identified as retardation elements, vanish when
the interaction between subunits is assumed to be instantaneous, instead of proceeding
at the speed of light.

Address of McClain and Ghoul: Department of Chemistry, Wayne State University,
Detroit, Michgian 48202

FC2.   (8:47)

RESONANCE RAMAN SPECTROSCOPY OF TRANSIENT RADICAL CATIONS

G.N.R. Tripathi

     The time-resolved resonance Raman technique for structural
and kinetic studies of transient cation radicals, prepared by
pulse radiolytic methods, will be discussed. By electron pulse
irradiation of aromatic molecules solvated in halo-alkanes
sufficiently high concentration ($\sim 10^{-4}$ M) of radical cations can
be produced in a few nanoseconds to facilitate their Raman
observation. The resonance Raman spectrum of diphenylbutadiene
cation radical obtained by this method will be presented.

Address: Radiation Laboratory, University of Notre Dame, Notre
         Dame, IN 46556

FC3.   (9:04)

HIGH-RESOLUTION CARS MEASUREMENT OF RAMAN LINEWIDTHS OF DEUTERIUM

David A. Russell and Won B. Roh

A cw coherent anti-Stokes Raman spectroscopy(CARS) system based on single-
mode Ar-ion and ring dye lasers has been used to obtain high-resolution
spectra of deuterium molecule. Accurate measurements of Raman linewidths
of deuterium have been made for pressures ranging from 1 to 20 atm.
Pressure broadening coefficients determined from the data for five
vibrational Raman transitions Q(0) through Q(4) are presented.

Address of Authors: Department of Engineering Physics, Air Force Institute
of Technology, Wright-Patterson AFB, OH 45433

FC4. (9:16)

VIBRATIONAL ASSIGNMENTS FOR THE LOW FREQUENCY RAMAN ACTIVE PHONONS IN TCNQ SINGLE CRYSTALS

K. M. WHITE, K.-H. BROSE, AND C. J. ECKHARDT

A satisfactory assignment for the low frequency, Raman active phonons of 7,7,8,8-tetracyanoquinodimethane (TCNQ) in the solid state has eluded spectroscopists ever since the first polarized Raman spectra of the single crystal were reported.[1] Several attempts have been made to assign the observed transitions as either intramolecular vibrations or lattice phonons, but it has been thought that significant coupling prevents a well defined demarcation in frequency between the internal and external modes in the TCNQ crystal.

In order to resolve this problem, we have measured the single crystal Raman spectra of TCNQ in the range 5-190 cm^{-1} for six different polarization configurations. The data exhibit some significant differences from results that have already been reported, particularly for the bands observed at 40, 63, and 75 cm^{-1}. A lattice dynamical calculation using a minimized potential for the TCNQ lattice has also been performed. A comparison of the theoretical and experimental results shows excellent agreement and offers a complete determination of the lattice phonon frequencies, symmetries, and eigenvectors of TCNQ.

[1]A. Girlando and C. Pecile, Spectrochim. Acta, 29A, 1859 (1973).

Address of White, Brose, and Eckhardt: Department of Chemistry, University of Nebraska, Lincoln, Nebraska, 68588-0304.

FC5. (9:33)

LOW TEMPERATURE MODULATED PIEZOREFLECTION SPECTRA OF TWO POLYDIACETYLENE SINGLE CRYSTALS: PTS AND DCHD

M. MORROW AND C. J. ECKHARDT

The electronic structure of polydiacetylene (PDA) crystals has resisted complete explanation. To gain further understanding, detailed analysis of their electronic spectra is desirable. Modulation techniques have proven very useful in the study of optical properties and molecular interactions in the solid state. In general, room temperature modulation spectra correlate with structure normally seen only in low temperature unmodulated spectra. To aid in the assignment of the PDA electronic structure and to answer the question of what enhancement of structure would be seen in low temperature modulation experiments, we have measured the piezomodulated reflection (PMR) spectra at 14K for the PDAs 2,4-hexadiyne-1,6-diol-bis(p-toluene sulfonate) (PTS) and 9,9'-(2,4-hexadiyne-1,6-diyl)bis-9H-carbazole (DCHD). These two PDAs show a strong 0-0 Frenkel exciton transition at 1.97 eV and 1.86 eV, respectively, followed by extensive vibrational side bands.

Structure due to intramolecular vibrations seen in the PTS and DCHD PMR spectra have been assigned. The values for the vibrational frequencies determined from the PMR spectra are in good agreement with those reported from Raman studies[1]. Also seen in the PMR spectra are low frequency modes which are associated with lattice modes. Furthermore, assignment of the transverse and longitudinal frequencies, corresponding to the maxima and minima in the PMR spectra, can be made and the stopping bandwidth for each band determined[2].

[1]D. N. Batchelder and D. Bloor, Advances in Infrared and Raman Spectroscopy Volume 11 (R. J. Clark and R. E. Hester, eds.), Wiley Heyden, 1984, p. 133

[2]T. Luty and C. J. Eckhardt, J. Chem. Phys., 81(1), 521 (1984)

Address of Morrow and Eckhardt: Department of Chemistry, University of Nebraska, Lincoln, Nebraska, 68588-0304

FC6.   (10:10)

SURFACE-ENHANCED RAMAN SPECTROSCOPY OF BILIRUBIN

You-Zung Hsieh and Michael D. Morris

We have investigated the surface-enhanced Raman spectroscopy of bilirubin and its albumin complexes on silver colloids. The di-carboxylate anion is the SERS active species. Adsorption on silver stabilizes the system against photodecomposition, allowing close approach to electronic resonance. Strong enhancement of in-plane ring modes suggests binding through carboxylates, with rings oriented normal to the silver surface. The intense SERS signals obtained with albumin complexes, and the small frequency differences suggest that one or both dipyrrole rings remain bound to albumin in the SERS-active molecules.

Address of Hsieh and Morris: Department of Chemistry, University of
Michigan, Ann Arbor, MI 48109.

FC7.   (10:27)

SURFACE-ENHANCED RAMAN SPECTROSCOPY OF FLAVINS AND FLAVOPROTEINS

Nam-Soo Lee and Michael D. Morris

The $N(3)$ anions of flavins are shown to be responsible for surface enhancement of Raman spectra on silver colloids. Studies of $N(3)$ substituted flavins, $N(3)$ deuterated flavins and pH effects will be discussed. The anion requires direct contact with the silver metal surface for enhancement. Their orientation is shown to be perpendicular to the metal surface. SER spectra from flavoproteins arise from released flavins by dissociation, not from the intact flavoproteins. SERS on colloids is shown to be a useful chemical diagnostic for traces of free flavins in solution with limited applicability to study of flavoproteins.

Address of Lee and Morris: Department of Chemistry, University of
Michigan, Ann Arbor, MI 48109.

FC8.   (10:44)

Surface Enhanced Raman Spectra from Flavins Adsorbed on a Silver Electrode: Observation of un-stable semiquinone intermediate

J. Xu, R. L. Birke and J. R. Lomdardi

The surface enhanced Raman scattering (SERS) spectroscopy of protein-free flavin in different redox states was investigated at a silver electrode. Good quality SERS spectra of oxidized flavin with an excitation frequency within the flavin absorption band (488 or 514.5 nm) and out of the absorp-tion band (yellow-red region) are reported. Fluorescence interference from the flavin is nearly com-pletely quenched by the surface interaction.

The flavin molecules were determined to be bound at the silver surface via its N_5 and O_4 atoms based upon the results of N_3-H deuterium substitution, effect of pH and electrolyte type on SERS spectra, and the SERS spectral analysis. Reduced flavin did not exhibit a well defined SERS spectrum probably because of the break down of the surface complex. The SERS spectra of neutral semiquinone radical, as an intermediate of the two single electron reduction steps, were observed in acidic solution with yellow or red excitation. This is the first time that the SERS spectroscopic technique has been used for probing the existence of the unstable intermediate species at the electrode surface.

Address of all authors: Department of chemistry, city college of New York, New York, N.Y.10031

FC9. (10:56)

VIBRATIONAL SPECTRA AND CONFORMATIONS OF CYCLOHEXYLPHOSPHINE AND 2-CYANOETHYLPHOSPHINE

V. F. KALASINSKY AND T.-H. PAI

Infrared spectra of gaseous and solid cyclohexylphosphine and Raman spectra of the condensed phases of this compound have been recorded. Data for the most stable conformer are consistent with the microwave results[1] which indicate the existence of a gauche-equatorial chair form. Additional conformations whose very weak lines in the room-temperature Raman spectrum are absent in the solid state have been observed and are at least 900 cal/mole less stable. The possible identities of these conformers will be discussed. Infrared and Raman spectra have likewise been recorded for 2-cyanoethylphosphine. There are two bonds about which internal rotation can give rise to conformers, and at least two, separated by approximately 300 cal/mole, have been observed. The number of depolarized lines in the Raman spectrum tentatively suggests that one of these is the C_s conformer (Tt). The identities of the conformers will be discussed.

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[1] Y. S. Li, 40th Symposium on Molecular Spectroscopy, Ohio State University, June 17-21, 1985, paper TG5.

Address of Kalasinsky and Pai: Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762.

FC10. (11:13)

INFRARED AND RAMAN BAND SHAPES AND MOLECULAR DYNAMICS IN LIQUID PICOLINES

J. SOBHANADRI

Infrared and Raman vibrational bands of the esters of crotanic acid and picolines are used to compute the respective correlation functions. Both short time and long time behaviour of the correlation functions are examined and compared with the correlation functions of the freely rotating molecule. For the picolines, three distinct bands are observed in the region 15-120 cm^{-1} and three relatively strong bands in the region 120-450 cm^{-1}. The various contributions to the band shape are discussed in the light of the earlier NMR and dielectric data and the present IR and Raman data.[1-3]

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[1] T.S. Natarajan, J. Gowrikrishna and J. Sobhanadri, Chem. Phys. Letts. 106, 211 (1984).
[2] J. Gowrikrishna, T.K.K. Srinivasan and J. Sobhanadri, J. Mol. Liquids, 28, 207 (1984).
[3] J. Gowrikrishna and J. Sobhanadri, Ind. J. Pure & Appl. Phys. 22, 599 (1984).

Address of Sobhanadri: Department of Physics, Indian Institute of Technology, Madras, India and Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556.

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41ST. MOLECULAR SPECTROSCOPY SYMPOSIUM AT THE OHIO STATE UNIVERSITY

JUNE 16-20, 1986

	MONDAY, JUNE 16TH	TUESDAY, JUNE 17TH	WEDNESDAY, JUNE 18TH	THURSDAY, JUNE 19TH	FRIDAY, JUNE 20TH
	9:15 A.M.--NOON	8:30 A.M.--NOON	8:45 A.M.--NOON	8:30 A.M.--NOON	8:30 A.M.--NOON

Morning Sessions

AUDITORIUM McPHERSON HALL

MA. PLENARY SESSION
T. OKA
C. W. MATHEWS
COBLENTZ AWARD &
LECTURE (11-12 noon)
Joel Harris

WA. PLENARY SESSION
G. Herzberg
Alan Carrington
E. W. Schlag

ROOM 1153 PHYSICS LAB

TA. MICROWAVE (Walter Gordy Memorial)

RA. ELECTRONIC THEORY
K. Morokuma (Invited)

FA. IONS

ROOM 1009 PHYSICS LAB

TB. IR INTENSITIES

RB. INFRARED

FB. ENERGY TRANSFER

ROOM 1005 PHYSICS LAB

TC. ELECTRONIC (Large Molecules)

RC. CIRCULAR DICHROISM

FC. RAMAN

ROOM 1005 CHEMICAL LAB

RD. MICROWAVE
RD'. ELECTRONIC (Polyatomic)

Afternoon Sessions

1:30-5:00 P.M.	1:30-5:00 P.M.	1:30-2:15 P.M.	1:30-5:00 P.M.

ME. INFRARED (Ions & Other Molecules)

TE. INFRARED

WE. R. N. Zare (PLENARY)
2:30-4:15 P.M.
WE'. VIBRATIONAL ANALYSIS

RE. IONS

MF. ELECTRONIC (Diatomics)

TF. COMPLEXES

WF. INFRARED THEORY

RF. ATMOSPHERIC INTEREST (H_2O, O_3, NO_2)

MG. ATMOSPHERIC INTEREST (CO_2)

TG. ELECTRONIC (Small Molecules)

WG. ELECTRONIC (Ions & Large Molecules)
4:30 P.M.
DEDICATION OF LASER FACILITY

RG. MICROWAVE

MG'. MATRIX

RH. POTENTIALS & ELECTRONIC (Small Molecules)

END

12-86

DTIC